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ACID AND BASE BINDING CAPACITIES AND VISCOSITY RELATIONS IN CERTAIN WHITEWARE CLAYS*

By Edward C. Henry† and Nelson W. Taylor

Abstract

In studying the relationships between the chemical and the physical behavior of clay slips, correlations otherwise obscured are brought out if the clay is first carefully purified. Electrodialysis seems to be an effective method of removing interfering adsorbed electrolyte from clay in preparing it for such investigations.

Electrodialyzed samples of several whiteware clays in wide use in the ceramic industry were found to behave chemically as weak acids and bases. The amount of NaOH necessary to neutralize the "acids" coincided with the smallest amount sufficient to produce the minimum viscosity in suspensions of these clays.

The p_H of exchange neutrality of each clay agreed closely with a maximum in its p_H-viscosity curve. At this point, the addition either of HCl or NaOH reduced the viscosity, although not equally. As further amounts of NaOH were added, two effects were recognized. Some clays continued to become more fluid until complete deflocculation, while other clays passed first through a range of concentration in which NaOH caused increasing viscosity. Changes in viscosity were observed also in suspensions with increasing concentrations of HCl. A theory for these effects is presented.

I. Introduction

The object of the investigation was to discover possible correlations between the chemical properties of ceramic clays and their flow behavior in thin slips. This involved (1) the determination, by titration curves, of the ultimate p_H, p_H of exchange neutrality, and cation or base exchange capacity of each clay and (2) a study of the effect of p_H on the apparent viscosity of clay slips having a fixed clay-liquid ratio.

The clays investigated were selected because of their long use in whiteware and allied branches of the ceramic industry and their wide variation in plasticity, or working properties. They were (1) North Carolina kaolin, Harris Clay Co., Spruce Pine, N. C.; (2) Georgia kaolin (Cherokee clay), R. T. Vanderbilt Co., New York, N. Y.; (3) Florida clay (E. P. K.), Edgar Bros. Co., Metuchen, N. J.; (4) Tennessee ball clay No. 7, Kentucky-Tennessee Clay Co., Mayfield, Ky.; and (5) Kentucky ball clay No. 4 (Old Mine), Kentucky-Tennessee Clay Co., Mayfield, Ky.

II. The Colloidal Nature of Clays

Soil chemists in recent years have shed much light on the chemical nature of the colloidal fraction of soils. Nearly all of this information is directly applicable to the study of the behavior of ceramic clays. These, although frequently containing but a small amount of material of small enough dimensions to be classed strictly as colloidal, exhibit in varying degrees many properties possessed by true colloids. Thus, clays show adsorption, flocculation and deflocculation, gel formation, and swelling under the influence of dilute electrolyte solutions; and individual clay particles in aqueous suspension assume a charge and migrate toward an electrode when subjected to the influence of a direct current.

Adsorption seems to be primarily a surface phenomenon, although at the same time it may be thought of as a chemical process. Originally believed to be solely a property of the colloidal portion of the clay, adsorption is now recognized as a function both of the amount of surface and the surface activity. As Meyer[1] pointed out, a clay composed of larger particles with very active surface might show this adsorptive power to a greater extent than a clay of smaller particles (and consequently greater surface area) having a less active surface.

The activity of the surface depends partly on its chemical composition. Mattson[2] found that the adsorption and exchange of cations at p_H 7

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† Prepared from material in a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, the Pennsylvania State College, 1936.

[1] W. W. Meyer, "Colloidal Nature and Related Properties of Clays," *Jour. Research Nat. Bur. Stand.*, **13** [2] 245–58 (1934); R. P. 706; *Ceram. Abs.*, **13** [11] 302 (1934).

[2] S. E. Mattson, "Laws of Soil Colloid Behavior: V, Ion Adsorption and Exchange," *Soil Sci.*, **31** [4] 313 (1931); *Ceram. Abs.*, **10** [8] 600 (1931).

by soil colloids in the same state of aggregation increases with increasing ratio of the acidoid to ampholytoid constituents of the colloid. "Acidoid" is a name applied to a colloid which reacts as an acid, such as colloidal silicic acid. Colloidal aluminum and ferric hydroxides are examples of "ampholytoids," colloids which can act either as acid or base depending on the environment.

It was originally thought that the clay fraction of soils, and also the material responsible for the plasticity of clays, was a single mineral, kaolinite. This belief was displaced by the hypothesis that the clay and soil particles of colloidal size were in the form of an amorphous complex, the composition of which could include any ratio of R_2O/SiO_2.

Recent X-ray studies, including those of Bray, Grim, and Kerr,[3] have shown crystallinity to extend far into the so-called colloidal range of particle sizes. A number of distinct kaolin and clay minerals have been identified such as nacrite, dickite, montmorillonite, beidellite, nontronite, and halloysite.

The more recent conception, as stated by Robinson,[4] is that the clay complex consists of a few minerals of definite crystal structure with which, in certain cases, free hydrated sesquioxides may be associated. Consequently, the adsorption or base-exchange capacity of a clay (called "saturation capacity" by Baver[5] and "capacity to bind bases" by Mattson[6]) may be a complex function of its surface area, chemical composition, and mineral constitution.

III. Electrodialysis

It has been recognized for many years that clays as mined are partly saturated with adsorbed ions whose presence has undoubtedly obscured the relationships sought in the numerous studies of the effect of electrolytes on the structure of ceramic clays.

The removal of these impurities, leaving the clay saturated with hydrogen and hydroxyl ions only, is accomplished, among other ways, in a three-compartment electrodialysis cell of the Mattson[7] type. Clay suspended in water is placed between two membranes, the pores of which are permeable to electrolytes but not to particles of colloidal size or larger. A direct current is applied, the electrodes being on opposite sides of the membranes from the clay. Soluble anions in the clay are attracted through the membrane to the positive electrode; the cations are pulled to the negative electrode compartment. The anions, usually sulfate, phosphate, or chloride, are replaced on the clay by OH ions; the monovalent and divalent cations are replaced by hydrogen from the water. In general, the number of cations displaced from the clay is far greater than the number of anions, which shows that in nature clay usually behaves as an anion or negative ion of a weak acid.

IV. Clays as "Colloidal Electrolytes"

Inasmuch as the exchangeable ions seem to be held to the clay particle by a kind of chemical bond, reactions involving base exchange and other considerations of the chemical activity of clays may be handled conveniently by treating the clay as though it were electrolytic in nature. Mattson[8] has recently emphasized the fact that the difference between colloidal acids, bases, and salts and ordinary electrolytes is primarily a difference in degree, not in kind. For purposes of calculation, explanation, and the development of theories, one can apply the mass-action concepts of solubility products and dissociation constants and generally describe the chemical behavior of clays in terms commonly used to describe that of ordinary weak electrolytes.

(1) Ultimate p_H

Electrodialyzed clay, having only H and OH ions adsorbed, may be expressed as H·clay·OH. From this complex, in aqueous suspension, H and OH ions may be thought of as dissociating until an equilibrium is reached. The hydrogen-ion concentration of this suspension is known as the "ultimate p_H." A clay with low ultimate p_H is therefore one with a strong tendency to ionize as an acid.

[3] R. H. Bray, R. E. Grim, and P. F. Kerr, "Application of Clay Mineral Technique to Illinois Clay and Shale," *Bull. Geol. Soc. Amer.*, **46**, 1909–26 (1935); *Ceram. Abs.*, **15** [5] 163 (1936).

[4] G. W. Robinson, Soils, Their Origin, Constitution and Classification. D. Van Nostrand Co., London and New York, 1932; *Ceram. Abs.*, **12** [2] 79 (1933).

[5] L. D. Baver, "Effect of the Amount and Nature of Exchangeable Cations on the Structure of a Colloidal Clay," *Univ. of Mo. Agric. Expt. Sta. Research Bull.*, No. 129 (1929).

[6] S. E. Mattson, "Neutral Salt Reaction in Relation to the Point of Exchange Neutrality, the Saturation, and the Combining Capacity of a Soil," *Lantbruks-Högskol. Ann.* [Uppsala], **2**, 135–57 (1935).

[7] S. E. Mattson, "Electrodialysis of Colloidal Soil Material and Exchangeable Bases," *Jour. Agric. Research*, **33**, 553–67 (1926).

[8] S. E. Mattson and Yngve Gustafsson, "Laws of Soil Colloid Behavior: XVIII, Colloidal Electrolytes," *Soil Sci.*, **43** [6] 421–52 (1937); *Ceram. Abs.*, **16** [9] 286 (1937).

(2) Combining Capacity

The exchange or combining capacity of a clay for a given cation is usually expressed as the number of equivalents of that ion held by 100 grams of clay saturated at a specified p_H. One method of determining the capacity is to titrate electrodialyzed or "acid" clay with the hydroxide of the cation in question, noting the amount required to bring the suspension to a given p_H, such as 7.0 or 8.0, or titrating to an inflection in the titration curve. The curves obtained are typical of the neutralization curves of a weak acid and a strong base. The reaction may be expressed as

$$H\cdot clay\cdot OH + KOH = K\cdot clay\cdot OH + H_2O.$$

Clays probably also exchange anions according to the equation

$$H\cdot clay\cdot OH + HCl = H\cdot clay\cdot Cl + H_2O.$$

(3) Neutral Salt Reactions

Mattson[9] has defined the p_H of exchange neutrality as the p_H of a clay suspension which is unaffected by the addition of a neutral salt. At this point the clay exchanges an equal number of OH and H ions for the anions and cations of the salt, as given by the equation

$$H\cdot clay\cdot OH + NaCl \rightleftarrows Na\cdot clay\cdot Cl + H_2O.$$

Clay shows an amphoteric nature in this respect. If clay is added to a salt solution whose p_H lies above the point of exchange neutrality, a displacement of the H ions by the cations of the solution will predominate, resulting in a lowering of the p_H (exchange acidity) according to the following equations:

$$H\cdot clay\cdot OH + NaOH \rightleftarrows Na\cdot clay\cdot OH + H_2O$$

and

$$H\cdot clay\cdot OH + NaCl \rightleftarrows Na\cdot clay\cdot OH + HCl.$$

Exchange alkalinity results when clay is added to a salt solution whose p_H lies below the point of exchange neutrality, as shown by the equations

$$H\cdot clay\cdot OH + HCl \rightleftarrows H\cdot clay\cdot Cl + H_2O$$

and

$$H\cdot clay\cdot OH + NaCl \rightleftarrows H\cdot clay\cdot Cl + NaOH.$$

The p_H of exchange neutrality is the point at which the tendency of the cations of the added salt to displace the H of the clay is equal to the tendency of the anion of the salt to displace the OH ions. It should not be confused with the isoelectric point, at which the anions and cations of the clay are dissociated equally when there are no displacing ions present. The point of exchange neutrality is affected by the relative power of the anions and cations of the salt solution to displace H and OH from the clay, this power being determined by the dissociation constants (or solubility, if considered that way) of the compounds which the anions and cations may form with the clay complex. For this reason, it is necessary to name the salt used in determining the point.

The point of exchange neutrality is found experimentally by titrating the clay with acid and base in distilled water and in a salt solution. Two curves are obtained which intersect at the p_H at which the salt, as a whole, produces no apparent effect.

V. Experimental Methods

(1) p_H Measurements

The most satisfactory method of measuring the p_H relationships in the clays seems to be the hydrogen electrode. Quinhydrone, although quicker and simpler, is subject to some criticism as it may react with the unsaturated clay. More important, however, is the fact that it can not be used above p_H 8, or at most 9, while it was planned to investigate suspensions with much higher p_H. Colorimetric methods were not considered satisfactory in view of the use of turbid suspensions frequently approaching a paste in consistency. There is doubt as to the accuracy of measuring the p_H of slips by determining the p_H of their extracts out of contact with clay. Bradfield[10] showed that the concentration of hydrogen ions in a clay paste may be 1000 times as great as that in the ultrafiltrate from such a paste.

Electrode vessels of the type developed by Bailey[11] were blown of Pyrex-brand glass. The advantage of this vessel is that the hydrogen enters at the bottom, and the stream of bubbles serves to stir the clay and keep it in suspension. The experience of workers in soil research argued against obtaining titration curves by adding increments of acid or base to the clay and measuring

[9] (*a*) S. E. Mattson and Kwang-Chiung Hou, "Equi-Ionic Point and Point of Exchange Neutrality of Soils," *Lantbruks-Högskol. Ann.*, **4**, 188 (1937).
(*b*) "The Laws of Soil Colloid Behavior: XX, Neutral Salt Effect and Amphoteric Points of Soils," *Soil Sci.*, **44** [2] 161 (1937); *Ceram. Abs.*, **17** [1] 43 (1938).

[10] Richard Bradfield, "Concentration of Cations in Clay Sols," *Jour. Phys. Chem.*, **36**, 340 (1932); *Ceram. Abs.*, **11** [5] 330 (1932).

[11] E. H. Bailey, "Effect of Air Drying on Hydrogen-Ion Concentration of Soils of the United States and Canada," *U. S. Dept. Agric. Tech. Bull.*, No. 291 (1932).

the p_H. Although Hardy and Lewis[12] stated that there is little to be gained by continuous shaking beyond three minutes after each increment is added, Clark and Collins[13] concluded that in titrating to p_H 7 with shaking, 90 hours is usually required for equilibrium to be attained. Denison,[14] titrating soil extracts to an inflection in the titration curve, found it was necessary to allow a period greater than 24 hours for the establishment of equilibrium between soil and sodium-hydroxide.

In view of these facts, titration curves were obtained by preparing a series of suspensions of clay and electrolyte, each of which would correspond to a single point on the curve. These were kept tightly stoppered in Pyrex-brand containers for 36 hours, during which time they received about 6 hours shaking before their p_H values were determined. This was evidently enough time, as several check suspensions tested after 50 hours agreed within 0.02 p_H unit.

(2) Flow Behavior

Nearly all known types of viscosimeters have been employed in studying the mobility and yield value, *i.e.*, the plastic flow characteristics of ceramic clay suspensions, as reviewed by Hobson.[15] A Stormer viscosimeter was chosen because of its flexibility and the ease and rapidity of measurements. This is a concentric cylinder type of instrument. The outer, stationary cylinder forms part of the cup to contain the material under test; the inner rotating hollow cylinder is activated by weights hung on a cord. It is not an absolute viscometer, but a simple calibration with oils of known viscosity was sufficient to make the calculation of results in absolute units with satisfactory accuracy. The method of Higgins and Pitman[16] was used in plotting and calculating constants involved in the calibration curves.

[12] F. Hardy and A. H. Lewis, "A Rapid Electrometric Method for Measuring Lime Requirements of Soils," *Jour. Agric. Sci.*, **19**, 18 (1929).

[13] N. A. Clark and E. R. Collins, "Equilibrium between Soil and Electrolytes, and Its Influence upon Some Lime Requirement Methods," *Soil Sci.*, **29**, 417 (1930).

[14] I. A. Denison, "Methods for Determining the Total Acidity of Soils," *Bur. Stand. Jour. Research*, **10**, 413–26 (1933); R. P. 539.

[15] G. D. Hobson, "Viscometric Measurements of Clay Suspensions," *Jour. Inst. Petroleum Tech.*, **21**, 204 (1935); *Ceram. Abs.*, **14** [9] 227 (1935).

[16] E. F. Higgins and E. C. Pitman, "Measurement of Viscosity of Pyroxylin Solutions," *Jour. Ind. Eng. Chem.*, **12**, 587 (1920).

(3) Preparation of Clay Slips

A series of slips containing various amounts of NaOH or HCl was prepared for each clay, both in the electrodialyzed condition and as received. From burettes, $N/10$ acid or base was mixed with distilled water in Pyrex-brand Erlenmeyer flasks to give 100 cubic centimeters of the desired electrolyte concentration, into which 50 grams of pulverized air-dried clay was dropped.

Each flask was stoppered, placed in a shaker, and agitated for about three hours. Thirty-six hours later it was shaken again for several hours and tested in the viscosimeter. The hydrogen-ion concentration of the slip was determined immediately after its viscosity measurement. A few of the slips were such thick pastes that it was necessary to add distilled water, shake, and allow them to stand a few hours before determining the p_H. There was always an excess of solid phase present and the p_H did not seem to be changed much by this dilution.

(4) Significance of "Apparent Viscosity"

In plotting the results, it was found advantageous to evaluate the flow characteristics of the slips in terms of the apparent viscosity. Clay suspensions, unless very dilute, do not act as true viscous liquids in which there is a linear relation between the applied force and the resulting flow. Their behavior must be expressed in terms of a yield value and mobility. As Rieke and Tscheischwili[17] have shown, when electrolyte is added to a clay, both yield value and mobility may change. Hall[18] compared clays by comparing their yield values after adjusting the clay-water ratio until their mobilities were the same. It seemed simpler in this instance to maintain a constant clay-liquid ratio and to report the flow behavior of each slip in a single value that, to a certain extent, included both variables. The apparent viscosity is numerically equal to the viscosity that a Newtonian liquid (one with a zero yield value) would have if it had required the same time per 100 revolutions of the viscosimeter spindle when activated by the same weight, as did the clay slip. Many of the deflocculated slips

[17] R. Rieke and L. Tscheischwili, "Viscosity of Kaolin and Clay Suspensions Measured with Different Viscosimeters and the Effect upon It of Different Methods of Treating the Materials," *Ber. deut. keram. Ges.*, **17** [1] 1–46 (1936); *Ceram. Abs.*, **15** [9] 288 (1936).

[18] F. P. Hall, "Method of Measuring the Plasticity of Clays," *Bur. Stand. Tech. Paper*, No. 234 (1923).

showed no yield value and consequently were actually viscous liquids. If two suspensions have the same yield point, that with the lower mobility will have the higher apparent viscosity. Of two slips with the same mobility, that with the greater yield value will have the higher apparent viscosity.

VI. Experimental Results

(1) North Carolina Kaolin

The ultimate p_H of this clay was 3.6. Its base-exchange capacity was 2.3 milliequivalents per 100 grams of air-dried clay.* The p_H of exchange neutrality, as shown by the titration curves of Fig. 1, was 3.5, corresponding to the addition of $^1/_2$ m.e. of HCl to the electrodialyzed clay.

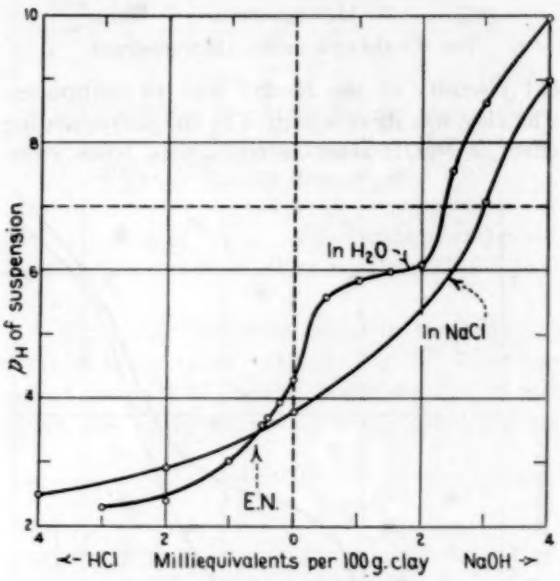

FIG. 1.—North Carolina kaolin.

The relationships of electrolyte content to the apparent viscosity and to the p_H of the clay are shown in Figs. 2 and 3. The former shows the behavior of the clay as received; the latter gives that of the electrodialyzed clay. With a constant viscosimeter load of 104 grams, the apparent viscosity of the untreated clay was 159 centipoises. This dropped steeply to about 42 on the addition of $^1/_2$ m.e. of NaOH and decreased more gradually to a value of 8 when 6 m.e. had been added.

The electrodialyzed or hydrogen clay had an apparent viscosity of 508 centipoises with the same viscosimeter driving force. The viscosity was reduced to 8 centipoises by the presence of $2^1/_2$ m.e. of NaOH, the amount required to bring the p_H of the suspension to 7.5, where the neutralization of this clay is completed.

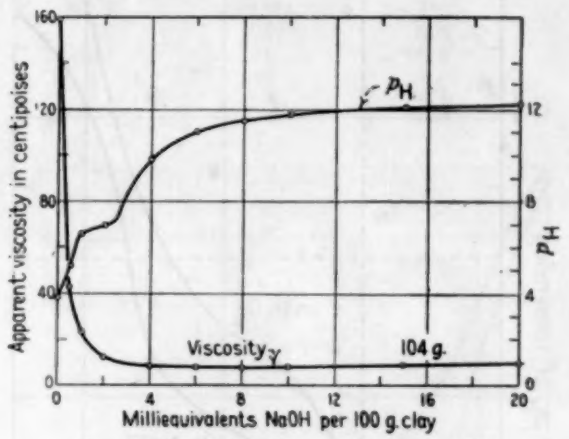

FIG. 2.—North Carolina kaolin, untreated.

With the addition of HCl to the hydrogen clay, the apparent viscosity dropped, rose to a peak in the presence of 2 m.e., dropped again with 3 and 4, and increased slightly on the addition of 5 and 6 m.e.

(2) Georgia Kaolin

From Fig. 4, the titration curves of electrodialyzed Georgia clay in water and in sodium-chloride solution, it is seen that the ultimate p_H was 3.4, the saturation capacity at p_H 7.0 was 5.6 m.e. of NaOH, and the point of exchange neutrality was at p_H 2.6, requiring the addition of $^2/_3$ m.e. HCl to the hydrogen clay. The inflection in the titration curve came between p_H 8.5 and 9.0 and indicated 7.0 m.e. NaOH for neutralization.

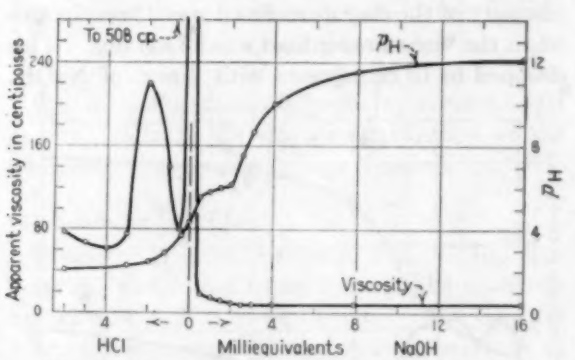

FIG. 3.—North Carolina kaolin, electrodialyzed.

* A milliequivalent is one-thousandth of a gram equivalent weight. One equivalent of NaOH being 40 grams, one milliequivalent is 0.040 gram. The abbreviation, m.e., will hereafter be used in this paper.

The titration curve in Fig. 5, for the clay "untreated," has but a slight inflection, indicating low buffer action in the clay which might have been highly saturated with cations in its recovery

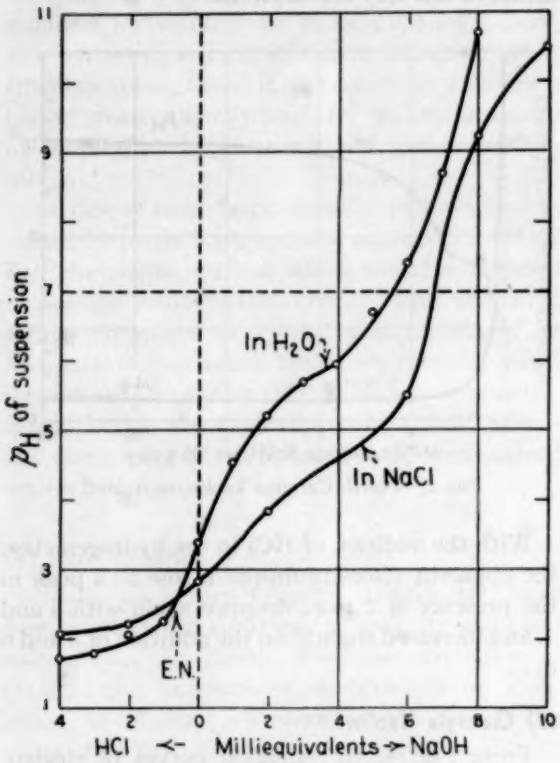

FIG. 4.—Georgia kaolin.

treatment before being shipped. The apparent viscosity of the clay as received was 22 centipoises when the viscosimeter load was 155 grams. This dropped to 10 centipoises with 2 m.e. of NaOH,

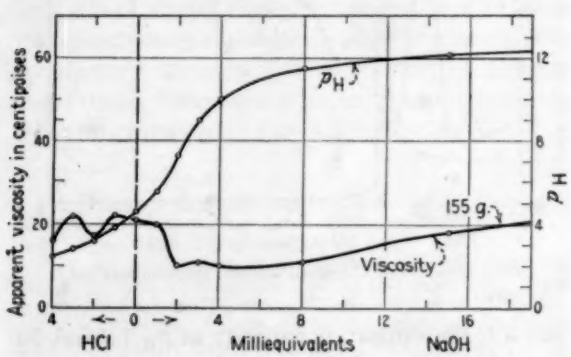

FIG. 5.—Georgia kaolin, untreated.

then gradually rose to a value of 21 with 20 m.e. On the acid side, there were two peaks at 1 and at 3 m.e. HCl and a minimum at or near 2 m.e. HCl.

The corresponding curves for electrodialyzed clay (Fig. 6) show similar relationships, greatly emphasized. The p_H-NaOH titration curve has a much more pronounced inflection. The apparent viscosity of the H clay was 49 centipoises. The clay was more sensitive to the deflocculating effect of NaOH after electrodialysis, 1 m.e. causing the viscosity to be reduced to 12 centipoises. This was increased to a maximum of 22 centipoises in 4 m. e. NaOH, dropped to 8 at 6 m.e., and remained constant in stronger alkali. The minimum was reached first as the p_H rose to 7.5, *i.e.*, when neutralization was nearly complete. On the

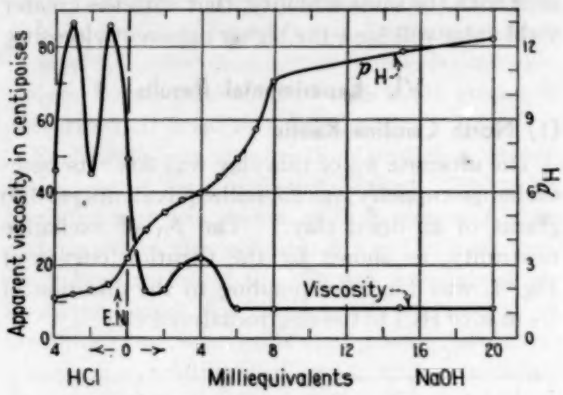

FIG. 6.—Georgia kaolin, electrodialyzed.

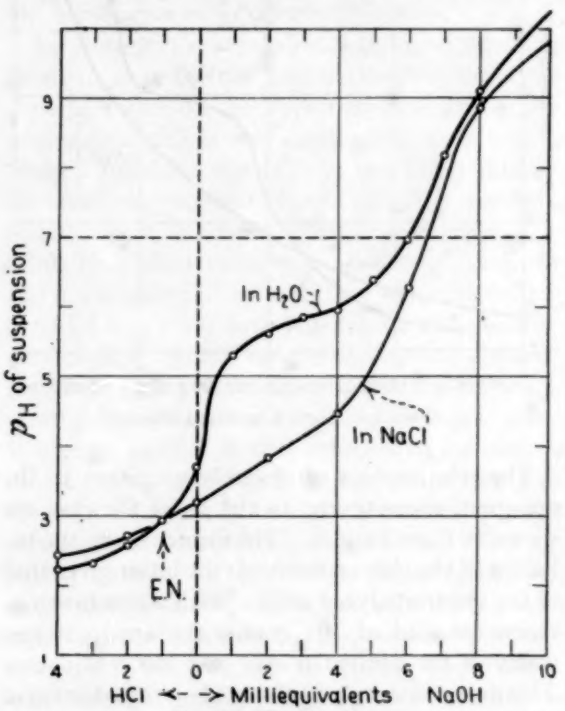

FIG. 7.—Florida clay.

acid side, the maxima and minima are much more pronounced than in the case of the untreated clay.

(3) Florida Clay

The titration curves in Fig. 7 show that the p_H of the hydrogen clay was 3.7, its base binding capacity at p_H 7 was 6 m.e., and its p_H of exchange neutrality was 2.95, a condition brought about by

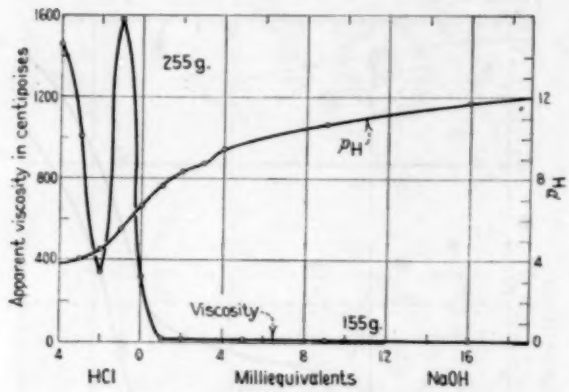

FIG. 8.—Florida clay, untreated.

adding 1 m.e. of HCl. The titration end-point for the clay was reached at p_H 7.8 with 6.7 m.e. of NaOH.

A slight inflection was found in the titration curve of the clay as received (Fig. 8). The apparent viscosity of the clay-water suspension was about 300 centipoises with a 255-gram driving

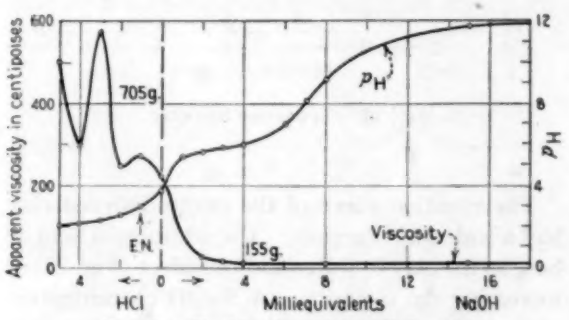

FIG. 9.—Florida clay, electrodialyzed.

force on the viscosimeter. The presence of 1 m.e. of NaOH caused a decrease to 11 centipoises (this time with 155 grams to drive the viscosimeter). The viscosity dropped further to 8 centipoises at 4 m.e., and slowly rose to 11 centipoises at 20 m.e. of NaOH. The addition of 1 m.e. of acid greatly stiffened the slip, 2 m.e. lowered it nearly to its value in water alone, and a further increase caused the viscosity to rise again.

Electrodialysis (see Fig. 9) changed the shape of the titration curve. The apparent viscosity-NaOH relationships, difficult to see on the graph, are tabulated as follows:

Milliequivalents NaOH	Apparent viscosity	p_H
2	24	5.6
3	17	5.8
4	10	5.95
8	8	9.1
20	10	12.0

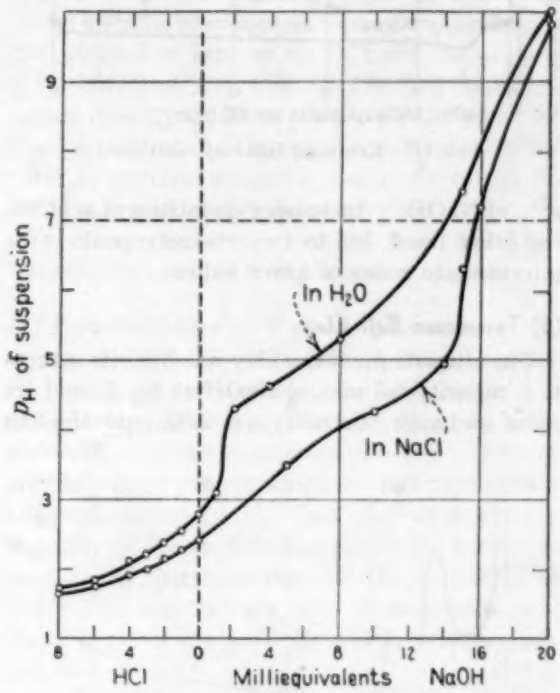

FIG. 10.—Kentucky ball clay.

The minimum viscosity probably occurred first at a p_H close to 7.8 when neutralization of the weak clay acid by NaOH was complete.

(4) Kentucky Ball Clay

From the titration curves in Fig. 10, the ultimate p_H was found to be 2.8 and the exchange capacity at p_H 7.0 to be 14 m.e. The clay did not become exchange-neutral within the range of p_H covered.

The apparent viscosity of the untreated clay in water was relatively low, 12 centipoises. Two milliequivalents of NaOH reduced it to $6^1/_2$ centipoises, from which point it was increased to 10 in the presence of 20 m.e. of NaOH (Fig. 11).

The electrodialyzed clay likewise had a low apparent viscosity in water. As shown in Fig. 12,

the lowest value, 6, coincided with an inflection in the titration curve at the unusually low p_H of 4.3. Another inflection occurred at about p_H 8 with 15

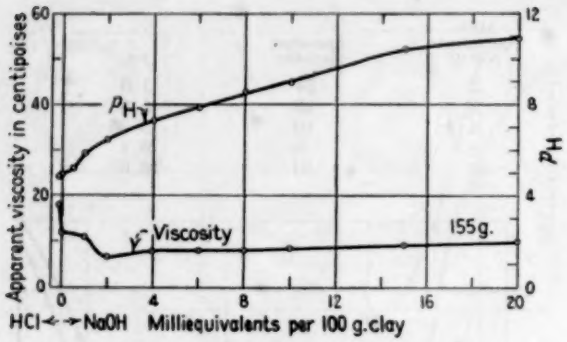

FIG. 11.—Kentucky ball clay, untreated.

m.e. of NaOH. Increasing quantities of acid, on the other hand, led to two viscosity peaks with intermediate zones of lower values.

(5) Tennessee Ball Clay

The ultimate p_H of this clay was 3.85, its saturation capacity 6.5 m.e. of NaOH at p_H 7, and its p_H of exchange neutrality was 2.50, equivalent to

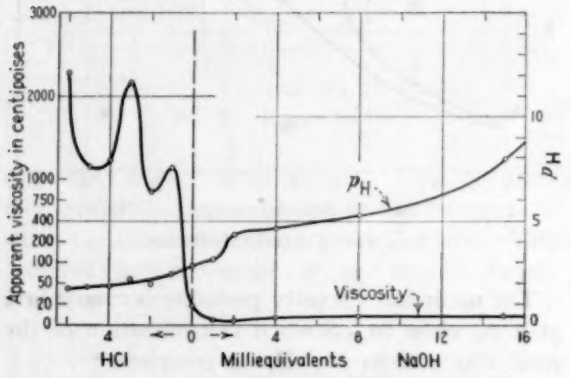

FIG. 12.—Kentucky ball clay, electrodialyzed.

the addition of 2 m.e. of HCl. The inflection in the titration curve in Fig. 13 came at p_H 8 with 7.2 m.e. of NaOH.

The titration curve of the untreated clay (Fig. 14) had a small buffer region. The first additions of NaOH served to increase the viscosity over that in water alone, the slip becoming stiff at p_H 6.25. At this point 2 m.e. of NaOH were present (in addition to ions introduced by the clay); the viscosity was estimated at over 40,000 centipoises, with a 455-gram driving load on the viscosimeter. With the same force, the viscosity in the suspension containing 3 m.e. of NaOH was calculated at 3000 centipoises. With 4 m.e., the viscosimeter load being reduced to 155 grams, the viscosity was measured as 450 centipoises. Viscosity was lowest (11 centipoises) when 8 m.e. had been added and increased to 40 in the suspension with 20 m. e. of NaOH.

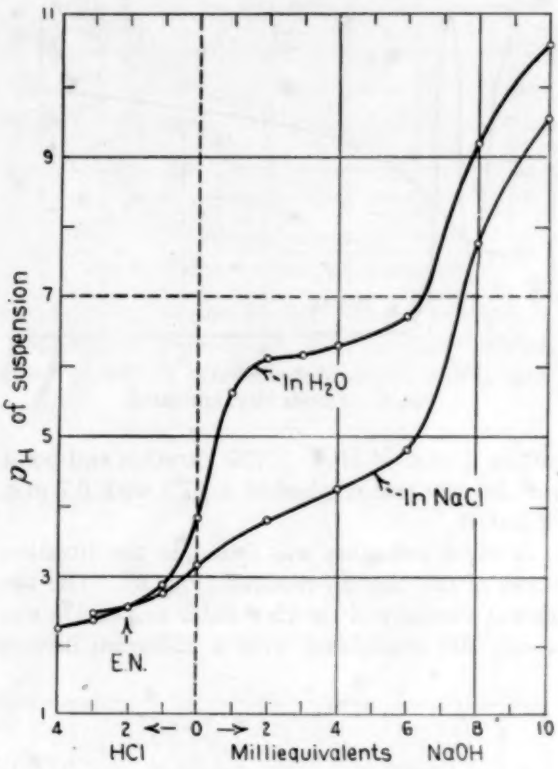

FIG. 13.—Tennessee ball clay.

The titration curve of the electrodialyzed clay had a wide buffer region. The addition of acid or base to the clay in water had the effect (Fig. 15) of increasing the viscosity. A NaOH concentration of 6 m.e. per 100 grams of clay produced a slip too stiff to be measured with the apparatus available. The viscosity was of the order of magnitude of 30,000 centipoises for a driving load of 700 grams. The suspension containing 8 m.e. of NaOH had a p_H of 9.2 and an apparent viscosity of only 7 centipoises (load 155 grams). This was increased to 8 at a p_H of 12.03 (20 m.e. of NaOH).

On adding acid to the electrodialyzed clay, two viscosity peaks were encountered, followed by a much greater increase in viscosity.

VII. Discussion of Results

Certain correlations and relationships appeared on consideration of the foregoing results:

(1) Electrodialysis, as would be expected, changed the properties of the clay in water and caused the apparent viscosity of the clay to be higher. In general, the clay was more sensitive

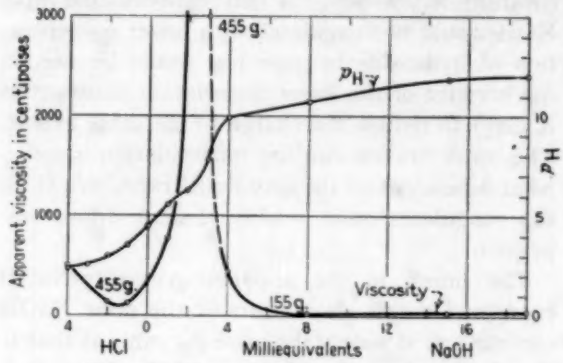

FIG. 14.—Tennessee ball clay, untreated.

to the effect of NaOH, reaching a low value of apparent viscosity, about 8 centipoises, at a lower p_H than before treatment. The titration curves are much sharper, with buffer regions lengthened or appearing where none had been shown before electrodialysis.

(2) There is a correlation between apparent viscosity and the titration curve of the clay with NaOH. In each electrodialyzed clay, a minimum viscosity was reached, usually sharply, but in the case of the Florida clay gradually, at a p_H corresponding to an inflection in the curve. If the clay is considered as a weak acid, this inflection marks the completion of its neutralization with the base. The situation was somewhat complicated in the case of the Kentucky clay. Here, two inflections were found, only the first of which was accompanied by a minimum of apparent viscosity.

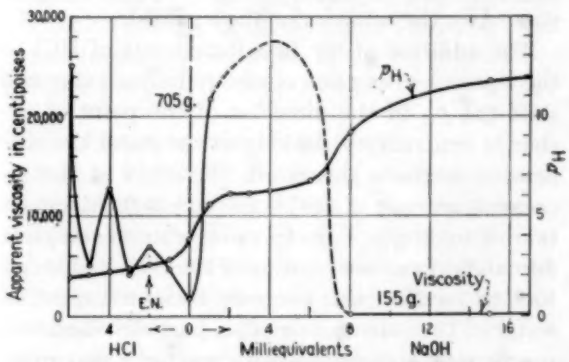

FIG. 15.—Tennessee ball clay, electrodialyzed.

This clay may be composed of two minerals of greatly different acid strengths, one of which is predominant in determining the viscosity change. In view of the absence of a point of exchange neutrality within the range of p_H studied, it is suggested that the first inflection may be attributed to free silicic acid or a silicate with high silica to sesquioxide ratio. Such material would not be expected to show an amphoteric nature in the p_H range studied.

(3) Two peaks in the apparent viscosity were found in acid suspensions, one corresponding to the addition of little or no HCl and the other to the addition of 2 to 4 m.e. The first maximum occurs directly at or very close to, the p_H of exchange neutrality, except in the Kentucky ball clay. This clay showed a maximum within the same p_H range as did the other clays, but its p_H of exchange neutrality was less than 1.6. This discrepancy is as yet unexplained.

(1) Probable Cause of Viscosity Changes

The viscosity of a suspension is largely a function of the relative volumes of solid and liquid, as discussed by Lewis and others.[19] The volumetric interference of the suspended particles will be increased by any process which will reduce the available suspending liquid. In a clay–water system, this may be accomplished either by the hydration of the clay particles through the formation of water films around them or by the enmeshment of water between the particles which constitute aggregates.

(*a*) *The Effect of NaOH:* The lowering of the apparent viscosity of electrodialyzed North Carolina, Florida, and Kentucky clays by sodium hydroxide is evidently the result of the deflocculation of aggregates of hydrogen clay and the liberation of occluded water.

For the Tennessee ball clay, the viscosity rises rapidly with progressive additions of NaOH and then drops to a very low value. This effect was noted by Baver, working with the colloidal fraction of Putnam silt loam, by La Rotonda,[20] also using colloidal clay, and by Mattson[21] with ben-

[19] W. K. Lewis, L. Squires, and W. Thompson, "Colloidal Properties of Clay Suspensions," *Trans. Amer. Inst. Mining & Met. Engrs.*, **114**, 38 (1935).

[20] C. La Rotonda, "The Physical Properties of Colloids," *Kolloid. Chem. Beihefte*, **35**, 553 (1926); *Ceram. Abs.*, **11** [10] 593 (1932).

[21] S. E. Mattson, "Laws of Soil Colloid Behavior: I," *Soil Sci.*, **28** [3] 216 (1929); *Ceram. Abs.*, **10** [4] 295 (1931).

tonite. The simplest explanation of this behavior would seem to be that the viscosity change this time is due to a change in particle size. By gradual neutralization and removal of hydrogen ions from the clay in the more alkaline solution, the charge and hydration of the clay micelles are increased and their total volume is larger. The same effect would result whether the swelling be of the osmotic type (sometimes referred to as undimensional swelling of the lattice), as reported by Endell[22] for montmorillonite, or an increase in the thickness of the water film around each charged particle.

The fact is significant that the swelling (and the apparent viscosity) is evidently at a maximum when the amount of sodium hydroxide present is but slightly less than sufficient to displace all the hydrogen from the clay. As soon as this maximum has been passed, when the titration curve begins to turn rapidly upward to mark the completion of the neutralization, the dissociation of the sodium-clay complex is partly repressed, as by a common-ion effect, with the result that the hydration, particle size, and apparent viscosity drop to a minimum coincident with the end-point of the titration. The effect of the common ion is to compress the Helmholtz double-layer and thereby to reduce the effective volume of the suspended particles. The phenomena may also be treated in terms of the Donnan theory of membrane equilibria.[23]

It would be expected, from analogy with the results obtained by Baver and many others, that, as the NaOH content of the suspension is further increased, a concentration of sodium ions will be reached sufficiently high to suppress the ionization of Na-clay particles to a low value and to reduce the charge on the particles below their critical potential. Slow coagulation would follow, and as aggregation proceeded water would be enmeshed between the particles, causing the suspension to become much stiffer. This effect was not observed with NaOH additions of 20 m.e. to electrodialyzed clay, although Baver found it when an amount of alkali more than three times the base-exchange capacity of the clay had been added. The flocculating effect of excess deflocculents in casting slips is well known. The extent of the deflocculation range when sodium salts are used is probably due to the large dissociation constant of Na clay. A clay deflocculated with KOH would be coagulated at a lower concentration of hydroxide because less would be needed (on account of the lower dissociation constant of K clay) to reduce the charge to the same extent. The concentration causing reflocculation is somewhat dependent on the clay-liquid ratio, as a thick slip coagulates more readily than a dilute suspension.

The hump in the apparent viscosity-NaOH curve of Georgia clay occurs at the same NaOH content and at nearly the same p_H value as that in the similar curve for Tennessee ball clay. It is believed that the Georgia clay may contain a sufficient quantity of the mineral responsible for such behavior in the Tennessee clay to cause this hump and that the lack of swelling in the other clays is due to the absence of this type of mineral. From analogy with the behavior of bentonite, one is led to suspect the presence of montmorillonite or a similar bentonitic mineral in the two clays showing swelling on the alkaline side.

(*b*) *The Effect of HCl:* Changes in the apparent viscosity on adding HCl to the electrodialyzed clay may have an explanation similar to that advanced for the behavior on the basic side.

The addition of the first increments of HCl to the aqueous suspension of electrodialyzed clay will shift the p_H in the direction of the point of exchange neutrality. As long as the p_H of the suspension is above this point, the effect of the increasing amount of acid is to repress the dissociation of hydrogen clay, to cause a more complete flocculation and coagulation of the clay, and therefore to increase the viscosity by entrapment of water. The charge on the particles becomes nearly zero, and the viscosity reaches a maximum at the point of exchange neutrality.

Further additions of acid may be thought of as gradually increasing the negative charge on the particles because Cl^- is adsorbed more than H^+ (as shown by the exchange alkalinity on this side of the point of exchange neutrality). Mutual repulsion leads to a breakup of some of the floccules and a lowered apparent viscosity. A point should

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[22] K. Endell, H. Fendius, and U. Hofmann, "Base Exchangeability of Clays and Forming Problems in Ceramics," *Ber. deut. keram. Ges.*, **15** [12] 595 (1934); *Ceram. Abs.*, **14** [6] 149 (1935).

[23] (*a*) F. G. Donnan and A. B. Harris, "Osmotic Pressure and Conductivity of Aqueous Solutions of Congo-Red and Reversible Membrane Equilibria," *Jour. Chem. Soc.*, **99**, 1554 (1911).
(*b*) F. G. Donnan, "Theory of Membrane Equilibria," *Chem. Rev.*, **1**, 73 (1924).
(*c*) H. R. Proctor and J. A. Wilson, "The Acid-Gelatin Equilibrium," *Jour. Chem. Soc.*, **109**, 307 (1916).

soon be reached, however, when the increasing swarm of chloride ions results in volume increases of the particles. From this point on, the increasing film around the clay particles will cause increasing apparent viscosity.

At still lower p_H, the chloride-ion concentration can be considered to have been so built up that common-ion effects will be important and will act to decrease the size of the micelle and the apparent viscosity of the whole system. This common-ion effect is analogous to that on the basic side. Progressively higher concentrations of chloride ions in the intermicellar solution suppress the charge to within the critical potential, where coagulation starts and viscosity rises rapidly.

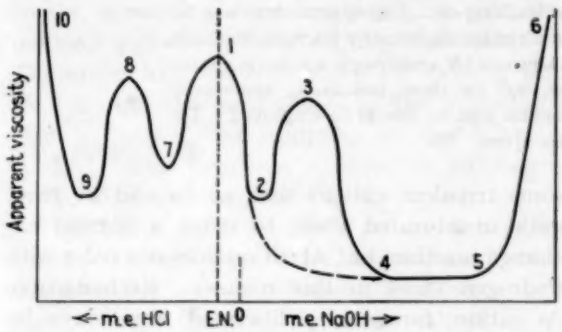

FIG. 16.

Some unpublished work in this laboratory has shown that the electric charge on the clay particles remains negative, although varying in magnitude, over the whole p_H range from 1 to 12. The minimum charge appears to be at the p_H of exchange neutrality.

(2) To Summarize the Discussion

Assume a clay to be at its p_H of exchange neutrality (*EN* in Fig. 16). As the p_H is increased, the viscosity drops (points (1) to (2)), owing to increased deflocculation and release of the water entrapped in the flocs of H clay. This behavior continues, in many clays and kaolins, to point (4) where the clay is completely deflocculated. In other clays, another factor which has been operating begins to make its presence felt at point (2). From this point, the viscosity tends to rise because the individual micelles are swelling (for reasons already given) and tends to drop to point (4) because of progressive deflocculation. If the clay is one in which the exchange of hydrogen by sodium causes much swelling, the viscosity will rise until a maximum is reached at point (3). Any further increase in NaOH concentration beyond (3) depresses the swelling, with a resultant steep drop in viscosity (to point (4)). There is a long deflocculation range from points (4) to (5). At point (5), the clay is reflocculated, and the viscosity rises. It is believed that the charge on the particles has been reduced by this concentration of NaOH to below the critical potential.

On the acid side of exchange neutrality, the clay seems to exchange and adsorb anions in the same manner that it does cations at higher p_H. Because of this and because of the apparent symmetry of the viscosity relationships, it is proposed that the explanation given for the viscosity behavior on the alkaline side of *EN*, based chiefly on experimental evidence of Mattson and Baver, be applied to the behavior on the acid side. The corresponding regions would then be from (1) to (7), deflocculation by increased charge; from (7) to (8), swelling of individual particles; from (8) to (9), depression of swelling by common-ion effect (and suppression of charge); and from (9) to (10), reflocculation, coagulation, and a large viscosity increase.

VIII. Summary

Three china clays and two ball clays, widely used in the whiteware industry, were purified by electrodialysis and were used for a study of the changes in p_H and viscosity as known amounts of NaOH or HCl were added, the clay-water ratio being fixed. Similar data were obtained on the untreated clays, which were more or less saturated with exchangeable acids and bases.

The electrodialyzed clays behaved as colloidal electrolytes, essentially as weak acids, although their amphoteric nature is shown by their ability to react with HCl. Their base combining capacity at p_H 7 ranged from 2.3 to 14 m.e. (0.09 to 0.56 gram) NaOH per 100 grams of clay.

Maximum deflocculation (minimum viscosity) was reached at the end-point of neutralization by base (base exchange or combining capacity).

Four of the clays showed a viscosity maximum at or close to the p_H of exchange neutrality, which ranged from 2.5 to 3.5. The Kentucky ball clay had a similar maximum in this range although its exchange neutrality was at a p_H less than 1.6.

THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA

CRITICAL STUDY OF METHODS OF DETERMINING EXCHANGEABLE BASES IN CLAYS*

By Robert P. Graham and John D. Sullivan

Abstract

A study was made of analytical methods of determining exchangeable bases in clays and similar ceramic materials. Total exchange capacity can be determined by electrodialysis or by the leaching-distillation method. The time required for electrodialysis can be materially reduced by agitation of the clay slip during dialysis. Electrodialysis effects decomposition of bentonite and similar materials unless extremely low current densities are applied. Exchangeable cations of clays and similar materials are replaced slowly by percolation methods, but an agitation leaching-centrifuging procedure was developed which effects a rapid replacement. In ultimate analyses by leaching methods, correction must be made for soluble sulfates. Aqueous 1*N* ammonium acetate is a satisfactory leaching solvent for most clay bodies, but for those containing appreciable amounts of calcium carbonate, alcoholic ammonium acetate should be employed. Details of recommended analytical procedures are given.

I. Introduction

During the past few years considerable attention has been given to base-exchange phenomena in clays.[1] For the most part, no critical studies have been made of the rôle of various bases, and most clays investigated have been converted either to the hydrogen or sodium form. In undertaking a study of the effect of exchangeable bases on clays, the writers desired to know the nature of the bases present in various clays and the effect of replacing the existing bases with others. The first problem comprised a critical examination of analytical methods to select a procedure combining reliability and speed. This paper, the first of a series on exchangeable bases in clays, considers analytical methods and recommends procedures applicable to clays and similar materials.

The phenomenon of base exchange is the replacement of bases or cations in or on a body by other cations. It can be expressed by the general formula,

$$cM^{a+} + aM_1^{c+} \rightleftarrows aM^{c+} + cM_1^{a+}.$$

The reaction is reversible for univalent and bivalent cations. Paver and Marshall[2] state that some trivalent cations such as La and Fe react with unsaturated clays to enter a normal exchange reaction, but Al cation does not react with hydrogen clays in this manner. Exchangeable Al cation, however, is liberated from clays by neutral salts, but H is simultaneously liberated.

Two distinct types of base-exchange reactions are recognized. The first, exemplified by all negatively charged colloids, is the simple replacement of one cation in the outer Helmholtz double layer by another cation. In the second type, cations of the crystal lattice are replaced by other cations which assume the geometric position of those displaced yielding a lattice with optical properties that differentiates it from the original. The two forms generally are regarded as distinct though isomorphous species.

II. General Methods of Determining Exchangeable Bases

Base-exchange determinations involve either that of total exchange capacity or of the individual exchangeable bases. Total exchange capacity is the sum of the metallic, hydrogen, and ammonium cations. Metallic cations may be determined as a group termed total metallic exchangeable bases, or the individual cations, Na, K, Ca, and Mg, may be determined. Because the amount of exchangeable Fe and Al is low and because some colloidal matter is likely to be carried in the leach solutions, analyses in the ultimate method are not made for these cations, and they are considered to be absent. In the proximate carbonate method described later in this paper for total metallic exchangeable bases, Fe and probably Al are included.

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* Presented at the Fortieth Annual Meeting, American Ceramic Society, New Orleans, La., March 27–April 2, 1938 (General Session on Clay Constitution). Received February 1, 1938.

Work done under Battelle Research Associate Fund.

[1] (*a*) K. Endell, U. Hofmann, and D. Wilm, "Nature of Ceramic Clays," *Ber. deut. keram. Ges.*, **14** [10] 407–38 (1933); *Ceram. Abs.*, **13** [4] 101 (1934).

(*b*) R. E. Grim, R. H. Bray, and W. F. Bradley, "Constitution of Bond Clays and Its Influence on Bonding Properties." *Trans. Amer. Foundrymen's Assn.*, **7** [5] 211–47 (1936); *Ceram. Abs.*, **16** [11] 329 (1937).

[2] H. Paver and C. E. Marshall, "Rôle of Aluminium in Reactions of Clays," *Chem. & Ind.*, **53** [36] 750–60 (1934); *Ceram. Abs.*, **15** [11] 346 (1936).

Total exchange capacity is determined by (*a*) electrodialysis or (*b*) replacement leaching. In the electrodialysis method, the material is converted to the hydrogen form which in turn is treated with varying amounts of standard alkali, and the p_H of the resulting slip or liquid is determined. Plotting the data yields an inflection point from which the exchange capacity is determined.

In the leaching method, the clay is converted to the ammonium form by treatment with ammonium acetate, $NH_4C_2H_3O_2$, or similar solution. The excess lixiviant is removed by washing with alcohol, and the ammonia from the ammonium clay is distilled, for example, by the Kjeldahl method. The ammonia distilled is equivalent to the total exchange capacity.

The $NH_4C_2H_3O_2$ leach liquor used in converting the raw clay to the ammonium form is analyzed for exchanged metallic bases. Raw clay treated by the Kjeldahl method gives exchangeable ammonium.

Total bases − (metallic + ammonium bases) = exchangeable H.

Various methods have been tried to determine exchangeable hydrogen directly. Schollenberger and Dreibelbis[3] leached soil with $NH_4C_2H_3O_2$ solution and titrated the pregnant solution with standard NH_4OH until the p_H of the solution equalled that of the original leach liquor.

In the leaching method, a large number of dilute salt and acid solutions have been used to determine exchanged bases and exchange capacity. Formerly ammonium chloride, NH_4Cl, was the principle reagent, and it is still used to a certain extent. Because it is acidic in nature and not strongly buffered, the results are not particularly reproducible. Alcoholic barium chloride has also found wide application and is particularly valuable for materials containing calcium carbonate, which is relatively insoluble in alcohol. Excess barium can be removed by precipitation as sulfate or chromate. Currently, the most widely used solution is 1*N* ammonium acetate which combines the following advantages: (1) solution is strongly buffered at a p_H of 7.0, (2) excess salt is destroyed on ignition, and (3) evaporation of leach liquor and ignition of residue leaves metallic exchanged bases as oxide or carbonate which can be titrated with standard acid.

The soil chemists have been foremost in work on base exchange, and quite satisfactory methods have been developed for most soils. Much of the technique used by soil chemists is not applicable to highly colloidal materials like clays. It was necessary, therefore, to study the methods used by previous investigators, to compare the accuracy of different methods, and to develop a method suitable for clays and similar ceramic materials.

III. Experimental Work

(A) Clays Used

The source and chemical analyses of clays used in this investigation are given in Table I.

TABLE I

CHEMICAL ANALYSIS OF CLAY BODIES

Clay	Ignition loss	Ingredient (%) SiO_2	Fe_2O_3	Al_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	S
Lawrence plastic	8.44	59.19	1.85	25.51	1.46	0.40	0.85	0.30	1.99	0.18
Ky. flint	13.53	44.35	1.41	37.36	2.04	0.28	0.58	0.47	0.55	0.14
Pa. flint	13.12	44.37	1.61	36.85	2.94	0.23	0.56	0.33	0.85	0.08
Ky. ball	12.88	51.85	1.65	29.79	1.44	0.32	0.63	0.22	0.75	0.05
Wyo. bentonite	6.04	63.64	4.13	18.92	0.28	0.81	2.41	2.47	0.43	0.16
Ga. kaolin (Wilkinson County)	13.77	44.71	0.90	38.60	0.51	0.15	0.32	0.07	0.14	Tr.

(B) Analysis by Electrodialysis

A sample of 200 grams clay or 100 grams bentonite was suspended in 700 to 800 cubic centimeters H_2O. Electrodialysis was carried out in a 3-compartment cell made of hard rubber. Each compartment measured $2^1/_2$ by 6 by 7 inches. The anode was a carbon plate and the cathode, sheet nickel. Each electrode measured 5 by 5 inches submerged area. The anolyte and catholyte compartments were separated from the dialysis compartment with parchment paper. At the start, water was placed in the two outside compartments, and the clay slip in the center one. Direct current was applied at 200 volts. The clay was kept in suspension by means of a mechanically rotated glass stirrer. The use of

[3] C. J. Schollenberger and F. R. Dreibelbis, "Analytical Methods in Base-Exchange Investigations on Soils," *Soil Sci.*, **30**, 161–73 (1930).

mechanical agitation eliminated the steps used by many previous investigators of carrying on the dialysis until the body was transferred to the anode diaphragm, removing the clay, drying, re-dispersing, and continuing the dialysis. As the electrodialysis progressed, the anolyte and catholyte were replaced at intervals with water. The total time of dialysis was 48 hours except for ball clay and bentonite for which the period was 72 hours. After the dialysis, the clay was dried at 105°C. One measure of the completeness of the dialysis was testing of the catholyte to determine when no additional alkali was removed from the body. In the case of bentonite, this was not complete even in 72 hours, and it is believed that it was decomposed by electrodialysis.

The electrodialyzed clays were dried at 105°C and broken to pass a 100-mesh Tyler sieve. Five-gram samples were transferred to a glass bottle and treated with varying amounts of standard NaOH in 20 cc. solution. With bentonite 1-gram samples were used. The bottle and contents were transferred to laboratory mixing rolls and agitated at 30 r.p.m. for 72 hours. The sample was then centrifuged to separate liquid and solids, and the p_H of the liquid was measured with

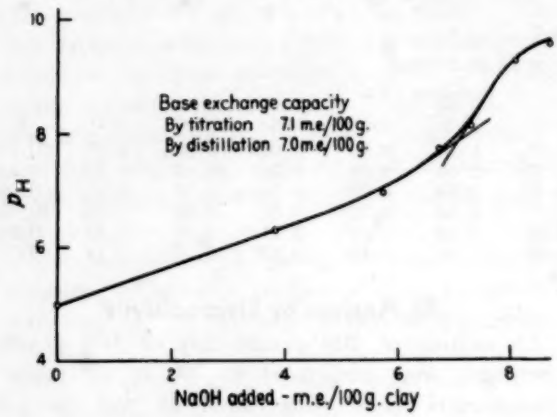

FIG. 1.

a glass electrode. The p_H was plotted *vs.* amount of base added, and the inflection point was taken as the neutralization of hydrogen clay, or base-exchange capacity. Figure 1 is a typical titration curve.

(C) Analysis by Leaching

The usual method of leaching employed by prior investigators comprised leaching the material in a porous container by percolation, usually downward. Percolation leaching was found to be too slow for use as a general analytical procedure. Clays were leached as long as three days, and the exchangeable bases were still not entirely replaced. Various modifications, including addition of filter paper and application of pressure, were ineffective in increasing materially the rate of extraction.

(1) Development of Leaching Procedure

The slowness of the percolation method led to an investigation for development of a more rapid leaching technique. The method finally evolved comprised leaching a 50-gram sample of clay or 25-gram sample of bentonite in a standard 250-cc. centrifuge bottle, $2^1/_2$ inches in diameter by 5 inches high, with 100 cc. 1*N* ammonium acetate ($NH_4C_2H_3O_2$). The sample and leach liquor were placed in the cup, and the upper end of the cup was closed with a rubber stopper. The closed container was agitated on revolving laboratory mixing rolls by rotating at 15 r.p.m. for a period of 30 to 40 minutes and then transferred to a size 1, type SB, International centrifuge and centrifuged at a rate of about 2000 r.p.m. until the solution became clear. This time varied from 10 minutes to 1 hour. The clarified solution was removed by decantation. Another 100 cc. leach liquor was added to the residue on the bottom of the centrifuge bottle, the mass was dispersed by shaking, and the agitation and centrifuging operations were repeated. Usually five successive washes were used. The solution can be used to analyze for exchanged bases. Apparently with many clays the replacement is completed during the first cycle, and subsequent ones are necessary only as washes. Experiments on a 10-gram sample of a plastic fire clay gave the following results:

	Milliequivalent/100 g. extracted
First wash	9.0
Second "	0.7
Third "	Trace

If the total base-exchange capacity was desired, the residue obtained from leaching with $NH_4C_2H_3O_2$ was treated with successive 100-cc. portions of 80% neutral C_2H_5OH by the same agitation and centrifuging procedure. Experiments showed, however, that for this determination the sample should be 20 grams for most materials and 5 grams for bentonite. Usually five 100-cc. washes were necessary, but the number varied

with the nature of the clay. The recommended procedure is to use at least four washes and to determine if any NH_4^+ is present in the last wash. This may be done quantitatively by the Kjeldahl method, but qualitative tests usually suffice. If NH_4^+ is present, continue the alcoholic washes until the solution is ammonia-free. The residue obtained in this manner can be analyzed for NH_4^+ by the Kjeldahl method, using NaOH or MgO as alkali.

(2) Analysis of Exchanged Metallic Bases

(a) Ultimate Method

Calcium: The exchanged bases can be analyzed by one of several methods. For many purposes, the ultimate method which gives Na, K, Ca, and Mg is necessary. The simplest method found in this investigation comprised evaporating the $NH_4C_2H_3O_2$ leach liquors to dryness, treating with 5 cc. concentrated HNO_3 to destroy organic matter, and evaporating to dryness. The residue was taken up with 10 cc. concentrated HCl and diluted to about 200 cc. The solution was neutralized with NH_4OH to precipitate any Al present, heated to boiling, and filtered. This filtration also served to remove any clayey material that might have been carried by the leach liquors. The solution was made slightly acid with HCl, 10 cc. ammonium oxalate solution (35.5 g./l. [0.5*N*]) was added, and the solution made slightly alkaline with NH_4OH to precipitate the Ca as CaC_2O_4. The solution and precipitate were heated to boiling, removed from the hot plate, allowed to stand one hour, and filtered. The precipitate was dissolved in 5 cc. 3*N* HCl, the solution diluted to 150 cc., 5 cc. $(NH_4)_2C_2O_4$ solution added, the solution made slightly alkaline with NH_4OH, the mass heated to boiling, removed from the hot plate, allowed to stand 1 hour, and filtered. The CaC_2O_4 was dissolved in 5 cc. concentrated H_2SO_4, diluted to 125 cc., heated to 90°C, and titrated with standard $KMnO_4$ solution.

The combined filtrates from the CaC_2O_4 precipitation were evaporated to dryness and treated with 25 cc. concentrated HNO_3 to destroy ammonium salts. The solution was evaporated to dryness, taken up in 50 cc. H_2O, and diluted to 100 cc. If any trouble was encountered in dissolving the residue in water, 5 to 10 cc. concentrated HNO_3 was added, and the solution evaporated to dryness. It was then taken up with 50 cc. water and diluted to 100 cc. Aliquots of 25 cc. each were taken for determination of Na and Mg, and 50 cc. for K.

Sodium: The Na was determined by evaporating the aliquot to dryness, and taking up in 1 cc. H_2O. Ten cubic centimeters zinc uranyl acetate solution* was added, and the solution was allowed to stand at room temperature for 12 hours to precipitate Na as $(UO_2)_3ZnNa(C_2H_3O_2)_9 \cdot 6H_2O$. The precipitate was filtered on a Gooch crucible and determined either gravimetrically or volumetrically. When the gravimetric process was employed, the precipitate was washed with three or four 1-cc. portions of C_2H_5OH saturated with $(UO_2)_3ZnNa(C_2H_3O_2)_9 \cdot 6H_2O$, and finally once or twice with ether. In the volumetric procedure, washing with ether was omitted, and in its place the final wash was made with about 0.5 cc. absolute C_2H_5OH. The Gooch crucible and contents were transferred to a beaker, excess standard sodium hydroxide solution added, the solution brought to boiling, and the excess NaOH back-titrated with standard acid, using phenolphthalein as indicator. The reaction may be written

$$(UO_2)_3ZnNa(C_2H_3O_2)_9 + 10NaOH = 9NaC_2H_3O_2 + Na_2U_2O_7 + ZnUO_4 + 5H_2O.$$

Potassium: The 50-cc. aliquot for potassium was treated with 5 cc. concentrated HNO_3, heated to boiling to decompose ammonium salts, and evaporated to dryness. The sample was taken up with 20 cc. water and evaporated to 10 cc., 10 cc. saturated NaCl solution, 10 cc. 10% cobaltous chloride solution, and 15 cc. 10% sodium nitrite solution added in the order given. The solution was evaporated to a pasty consistency on a steam bath, the mass cooled, and 10 cc. 10% acetic acid and 10 cc. H_2O added. The solution was filtered through an asbestos Gooch crucible and washed with $2^1/_2$% Na_2SO_4 solution. The total volume of wash solution should not exceed 25 cc. A measured excess of standard $KMnO_4$ solution was added to a beaker, and the Gooch crucible and precipitate were placed therein. The solution was diluted to 100 cc., 5 cc. concentrated H_2SO_4 added, and the solution was boiled to oxidize all nitrite. After boiling 10 to 15 minutes,

* (*A*) Uranyl acetate 85 g.; Glacial acetic acid 50 cc.; Water 400 cc. (*B*) Zinc acetate 200 g.; Glacial acetic acid 25 cc.; Water 250 cc. — Mix, let stand 24 hours, and filter immediately before using

the excess $KMnO_4$ was titrated with standard oxalic acid solution. The amount of K was calculated by the following empirical equation:

$$K_2O \text{ in mg.} = KMnO_4 \text{ value} \times 0.354 + \frac{(KMnO_4 \text{ value})^2 \times}{0.00034}$$

Where $KMnO_4$ value = cc. 0.05*N* $KMnO_4$ necessary to oxidize the precipitate.

Magnesium: Magnesium was determined in the 25-cc. aliquot by diluting to 150 cc., heating to 70 to 80°C, adding 10 cc. 2% 8-hydroxyquinoline solution in 2*N* acetic acid, neutralizing with NH_4OH, and finally adding 1 to 2 cc. excess 6*N* NH_4OH. The solution was set aside and allowed to cool and stand for 1 hour or longer. When the precipitate has settled, the supernatant liquid should be yellow, indicating an excess of reagent present. The solution was filtered through a No. 42 Whatman or equivalent filter paper and washed thoroughly with cold water. The precipitate was dissolved from the filter paper in about 25 cc., 2 to 2.5*N* HCl, the filtrate being caught in a glass-stoppered bottle and diluted to 50 to 75 cc. with the same acid. The reaction is

$$Mg(C_9H_6ON)_2 \cdot 2H_2O + 2HCl = MgCl_2 + 2C_9H_7ON + 2H_2O.$$

One gram KBr and 2 to 4 drops 0.1% methyl red solution were added to the solution, which was then titrated, by slowly adding standard potassium bromate solution until the color changed from red to yellow indicating an excess of bromate. The solution was constantly stirred during titration. Indigo carmine may also be used as indicator. The reactions are

$$KBrO_3 + 5KBr + 6HCl = 3Br_2 + 3H_2O + 6KCl.$$
$$C_9H_7ON + 2Br_2 = C_9H_6ONBr_2 + 2HBr.$$

When excess $KBrO_3$ was added as shown by the indicator color change, the bottle was stoppered, allowed to stand 2 minutes, and 1 gram KI was added. The liberated iodine was titrated with standard sodium thiosulfate solution. The reaction is

$$Br_2 + 2KI = 2KBr + I_2.$$

The zinc uranyl acetate method for sodium has been described in detail by Dobbins and Byrd,[4] the 8-hydroxyquinolate method for magnesium by Kolthoff and Sandell,[5] and the cobaltinitrite method for potassium by Piper.[6]

(b) Proximate Carbonate Method

In the proximate method, the $NH_4C_2H_3O_2$ leach liquors were evaporated to dryness and ignited to a dull red heat (about 500°C) to convert the exchanged bases to oxide or carbonate and to remove NH_4 salts. For simplicity, this method will be termed the proximate carbonate method. Standard HCl, approximately 0.1*N*, was added in excess, and the solution was cautiously heated to dissolve the exchanged bases. The excess acid was back-titrated with standard alkali. This method is essentially that described by Bray and Willhite,[7] but it was found preferable to carry out all operations in platinum rather than glass. The evaporations may be carried out in Pyrex-brand glassware, but ignitions should be done in platinum to avoid attack of the glassware. Glazed porcelain casseroles were badly attacked, and for that reason could not be used for ignition.

(c) Proximate Sulfate Method

The volumetric method for determining total exchanged metallic bases has been described. An alternative gravimetric method can be used. A 20-gram sample was leached in the usual manner, and the solution was evaporated to dryness and ignited in platinum. Preferably platinum should be used both in evaporation and ignition, but to save time the evaporation can be carried out in Pyrex-brand glass without introduction of serious error. The ignition was carried out at a relatively low temperature, no effort being made to destroy all carbon present. The residue was digested with 2 cc. concentrated H_2SO_4 to convert exchanged bases to sulfates, the excess H_2SO_4 was removed by fuming, and the residue was ignited to about 500°C to destroy carbon. The residue was treated with 5 cc. HF and 5 cc. 6*N* H_2SO_4 to remove SiO_2. The H_2SO_4 was removed by fuming. A second portion of H_2SO_4 was added, heated to remove SO_3 fumes, and ignited at about 700°C. The residue was taken up in 10 cc. con-

[4] J. T. Dobbins and R. M. Byrd, "Volumetric Method for Determining Sodium," *Jour. Amer. Chem. Soc.*, **53**, 3288 (1931).

[5] I. M. Kolthoff and E. B. Sandell, Textbook of Quantitative Analysis, pp. 609–10. The Macmillan Co., New York, 1936.

[6] C. S. Piper, "Volumetric Determination of Potassium by the Cobaltinitrite Method," *Jour. Soc. Chem. Ind.*, **53**, 392–96T (1934).

[7] R. H. Bray and F. M. Willhite, "Determination of Total Replaceable Bases in Soils," *Ind. Eng. Chem., Anal. Ed.*, **1** [3] 144 (1929).

centrated HCl, the solution diluted to 150 cc., filtered, and the SO_4 was precipitated as $BaSO_4$, filtered, and weighed.

(3) Determination of Exchangeable Hydrogen with Quinhydrone Electrode

One proposed method[8] of determining exchanged hydrogen comprises leaching with ammonium acetate solution and titrating the pregnant solution with standard NH_4OH until the p_H of the solution equals that of the original leach liquor. Schollenberger and Dreibelbis used a quinhydrone electrode but presumably other sensitive electrodes can be used. The writers' results by the Schollenberger and Dreibelbis method were erratic, owing to loss of NH_3 in the leaching and centrifuging operations. This method necessitates the use of closed containers.

(4) Determination of Exchangeable Ammonium

A 20-gram sample of raw clay was transferred to a standard 800-cc. Kjeldahl flask, 50 cc. 30% NaOH solution or 10 grams MgO and 150 cc. H_2O were added, the NH_3 was distilled into a measured excess of standard HCl, and the excess acid was back-titrated with standard NaOH, using brom cresol purple as indicator. The method is essentially the same as that employed for total exchangeable bases. No exchangeable ammonium was found in any of the argillaceous materials used in this investigation.

(5) Correction for Sulfates

In carrying out the methods outlined, the sum of the metallic exchanged bases by the ultimate method sometimes was higher than the total metallic exchanged bases by the carbonate proximate method. The magnitude varied with different clays. Experimental work showed that the difference in most cases was due largely to soluble sulfates extracted by the $NH_4C_2H_3O_2$. The correction for SO_4 was made by leaching a 20-gram sample in the usual manner or by taking a suitable aliquot of the solution used in the ultimate determination, evaporating the solution to dryness, and igniting at a low temperature to remove ammonium salts. The residue was dissolved in 10 cc. concentrated HCl, the solution diluted to 150 cc., and filtered, and the SO_4 precipitated as $BaSO_4$ in the usual manner. The correction must be applied to the ultimate method of analysis but not to the proximate carbonate because in the latter the sulfates present do not consume acid in titrating. Correction must also be made in the proximate sulfate method.

The fact that soluble metallic sulfates other than exchangeable bases may be extracted from clays, throws a doubt on the specific reliability of the ultimate method. It is believed, however, that for most clays the soluble sulfate exists largely as calcium sulfate and that if the exchanged calcium by ultimate analysis is corrected for the equivalent amount of total sulfate extracted, the analysis will not be greatly in error. For some materials, this correction can not be applied. Bentonites frequently contain sodium sulfate and possibly magnesium sulfate; so corrections for sulfate in them are only approximations.

Data are given in Table II on analysis of samples of Georgia kaolin and a plastic fire clay from Ohio to show the magnitude of sulfate corrections. Data are also given in Table V on bentonite.

TABLE II

EFFECT OF SULFATES ON PROXIMATE DETERMINATIONS

	Exchanged metallic bases (m.e./100 g.)			
	Georgia kaolin		Lawrence plastic fire clay	
Total metallic exchange determination	(not corrected)	(corrected)	(not corrected)	(corrected)
By ultimate analysis	1.2	1.1	9.6	7.4
By proximate carbonate method	0.9		7.7	
By proximate sulfate method	1.0	0.9	9.8	7.6
SO_4	0.1		2.2	

(6) Effect of Soluble Carbonates

In all of the materials studied, except bentonite, the agreement between total exchange capacity and total metallic exchangeable bases, when corrections for sulfate were made, was satisfactory. With bentonite the total metallic exchangeable bases were always higher than the total exchange capacity.

Burgess[9] and his co-workers showed that base-exchange reactions took place as readily in al-

[8] See reference 3.

[9] (*a*) P. S. Burgess and J. F. Breazeale, "Methods for Determining Exchangeable Bases of Soils, either in the Presence or Absence of Alkali Salts," *Ariz. Agric. Expt. Sta. Tech. Bull.*, No. 9 (1926).
(*b*) O. C. Magistad and P. S. Burgess, "Use of Alcoholic Salt Solutions for Determination of Exchangeable Bases in Calcareous Soils," *ibid.*, **20**, 481–97 (1928).

coholic as in aqueous salt solutions. They also showed that the amount of $CaCO_3$ and $MgCO_3$ dissolved was greatly reduced by use of alcoholic rather than aqueous solutions. Using 0.1*N* $BaCl_2$ in 68% C_2H_5OH, $CaCO_3$ was dissolved at 20°C to the extent of 15 p.p.m., whereas in water the dissolution was 72 p.p.m. With $MgCO_3$, the dissolution in 0.1*N* $BaCl_2$ in 68% C_2H_5OH and H_2O was 229 and 442 p.p.m., respectively.

The total exchange capacity of a sample of Wyoming bentonite, by the usual distillation method previously described, was 74.3 m.e. per 100 grams. The total metallic exchanged bases by the carbonate method was 87.6. The sample was leached with alcoholic 1*N* $NH_4C_2H_3O_2$, and the procedures were carried out in exactly the same manner as with the aqueous leach. The total exchange capacity was 73.8, the sum of the ultimate analysis for exchangeable metallic bases corrected for sulfate was 81.9, and the proximate carbonate analysis for total exchangeable metallic bases was 80.8. The total base-exchange capacity by the two methods of extraction agreed well, and inasmuch as the value was lower than by the proximate or ultimate methods either by alcoholic or aqueous extraction, the latter methods are believed to be in error. The error is likely due to soluble carbonates in the bentonite, particularly calcium and magnesium. The discrepancy between the distillation and ultimate or proximate methods was reduced by use of alcoholic leach liquors, but owing to the appreciable solubility of both $CaCO_3$ and $MgCO_3$ in C_2H_5OH, it is believed that the differences still present were due to this source of error. Qualitative analysis showed carbonate to be present. Chemical analysis, by combustion, disclosed about 0.1% of C.

A water suspension of the bentonite had a p_H of 9.8 and this combined with the relatively high CO_2 content makes the existence of exchangeable hydrogen doubtful.

(7) Precautions to Be Observed

In any of the methods of analysis, blank determinations should be carried through, and the blank corrections made.

With an unknown material, special attention should be paid to completeness of precipitation. When a reagent is added to effect precipitation, a few drops of reagent should be added to the supernatant liquid after the precipitate settles.

(D) Analysis of Typical Clay Materials

An analysis was made of clays varying from materials of low exchange capacity, such as kaolin, to bentonite of high capacity. Most of the materials studied slaked on addition of leaching solution, but flint clays did not slake materially. A study was made by the proximate carbonate method on the effect of particle size on total metallic bases extracted from two samples of flint fire clay. Data are given in Table III. All sizes were obtained by stage crushing and grinding.

TABLE III

EFFECT OF PARTICLE SIZE ON BASE EXCHANGE CAPACITY OF FLINT FIRE CLAYS

	Size (mesh Tyler)	Metallic base exchange (m.e./ 100 g. clay)
Ky. flint fire clay	− 28	6.2
	− 48	6.3
	−100	6.5
	−200	6.7
Pa. flint fire clay	− 28	4.5
	− 48	4.6
	−100	4.8
	−200	5.1

Data are given in Table IV on the analysis of five materials. All samples were minus 200-mesh size. In all cases the ultimate determination was corrected for leached sulfates on the assumption that they were all $CaSO_4$.

TABLE IV

ANALYSIS OF EXCHANGEABLE BASES OF FIVE MATERIALS BY VARIOUS METHODS

	Exchangeable metallic bases (milliequivalents /100 g.)				
Component	Ga. kaolin	Pa. flint fire clay	Ky. flint fire clay	Lawrence plastic fire clay	Ky. ball clay
Calcium	0.4	2.5	3.4	5.2	7.1
Magnesium	0.6	1.8	2.0	1.3	3.8
Sodium	0.1	0.5	0.9	0.4	0.5
Potassium	Trace	0.4	0.8	0.5	0.4
Sum	1.1	5.2	7.1	7.4	11.8
Determination	Total metallic exchangeable bases				
By proximate carbonate method	0.9	5.1	6.7	7.7	12.3
By proximate sulfate method	0.9	5.0	6.6	7.6	12.0
Determination	Base-exchange capacity				
By ammonia distillation	2.5	7.1	7.9	10.8	14.4
By electrodialysis	2.4	7.1	7.4	10.6	15.3
	Exchangeable hydrogen*				
	1.6	2.0	1.2	3.1	2.1

* (Base-exchange capacity by ammonia distillation) − (total metallic exchangeable bases by proximate carbonate method.)

Data on bentonite by various methods are given in Table V. The total exchange capacity by electrodialysis was low. Dialysis for 72 hours was not long enough to produce an alkali-free catholyte. There is general agreement that bentonite is decomposed during electrodialysis and that extremely low current densities must be used to minimize decomposition. If in the analysis for total metallic exchangeable bases the assumption is made that the Ca and Mg cations are from soluble salts and not exchangeable bases, the difference between total exchange capacity and metallic exchangeable bases is greatly reduced. For example, with the alcoholic leach the corrections lower the total metallic exchangeable bases to 74.8 m.e. per 100 grams.

TABLE V

BASE EXCHANGE ANALYSIS OF BENTONITE BY VARIOUS METHODS

Component	Exchangeable metallic bases (m.e./100 g.) By aqueous $NH_4C_2H_3O_2$	By alcoholic $NH_4C_2H_3O_2$
Calcium	18.4	10.1
Magnesium	4.9	4.9
Sodium	76.6	74.3
Potassium	0.5	0.5
Sum	100.4	89.8
Extracted sulfate	9.3	7.9
Sum corrected for sulfate	91.1	81.9
Total metallic exchangeable bases by proximate carbonate method	87.6	80.8
Base-exchange capacity by distillation	74.3	73.8
Base-exchange capacity by electrodialysis	57.0	

IV. Discussion of Analytical Methods

Total base-exchange capacity can be determined either by electrodialysis or leaching-distillation methods. The electrodialysis method requires less personal attention although the overall time required is longer. It also has the following disadvantages: (1) difficult to determine when dialysis is completed, (2) some materials such as bentonite may be decomposed, and (3) the inflection point in the p_H *vs.* NaOH curve not distinct.

The following advantages favor the leaching-distillation method: (1) relatively rapid, (2) not affected by soluble sulfates or carbonates, (3) titration is distinct, and (4) the solution can be used for analysis of exchanged cations.

Among the disadvantages are (1) careful washing with alcohol to remove $NH_4C_2H_3O_2$ necessary and (2) distillation must be watched carefully.

The method of determination of metallic exchangeable bases depends on whether individual cations or total metallic bases are required. The $NH_4C_2H_3O_2$ leaching method including correction for soluble sulfate, given earlier in this paper, is recommended for the ultimate method. Materials containing appreciable amounts of calcium carbonate should be leached with alcoholic $NH_4C_2H_3O_2$.

If only total metallic bases are required, the carbonate method is recommended. It is relatively rapid and is not affected by soluble sulfates. For best results, platinum should be used. Too high ignition temperatures must be avoided with colloidal material high in exchangeable magnesia because magnesium silicate which is insoluble in dilute acid is likely to form. For materials high in calcium carbonate, alcoholic rather than aqueous $NH_4C_2H_3O_2$ should be used for leaching.

The sulfate method of determining total metallic exchangeable bases is not so simple as the carbonate method, but it eliminates the tendency of errors due to formation of magnesium silicate. Correction must be made for soluble sulfates.

No satisfactory method can be outlined for the determination of individual exchangeable cations in bentonite and similar colloidal materials with extremely high exchange capacity. Leaching with alcoholic $NH_4C_2H_3O_2$ decreases the soluble salt error but does not eliminate it.

A sample of bentonite was leached with 80% C_2H_5OH, and 1.7 m.e. SO_4 and 3.1 m.e. Na were extracted per 100 grams. It is difficult to apply a correction from these data because the solubility of sulfates in C_2H_5OH probably is not the same as in 1*N* $NH_4C_2H_3O_2$ in 80% C_2H_5OH. In addition, if $MgSO_4$ is dissolved by C_2H_5OH, it may react with exchangeable Na because the exchange energy of Mg^{++} is greater than that of Na^+.

The leaching-distillation method gives a fairly true measure of total exchange capacity of bentonites.

V. Discussion of General Leaching Procedure

Clays and similar highly colloidal materials are not amenable to leaching by the usual percolation methods employed by soil chemists. Base-exchange reactions are rapid, and if contact of solids and lixiviant is maintained the time required for an analytical determination can be greatly reduced. Filtration of clay slips is slow and often ineffective. The agitation leaching and centrifuging method is recommended.

BATTELLE MEMORIAL INSTITUTE
COLUMBUS, OHIO

FRIT SOLUBILITY: II, CONTROLLED VARIABLES OF FRIT COMPOSITION AND THEIR RELATION TO ENAMEL CONSISTENCY*

By G. H. McIntyre and R. E. Bevis

Abstract

The sodium carbonate and borax of a sheet-steel ground-coat composition were varied to give variable frit solubility. Definite relationships between enamel consistency and Na_2O and B_2O_3 content of the mill liquor are shown. The ratio of soluble Na_2O to B_2O_3 is of more importance than their total solubility.

I. Introduction

The first work of the authors[1] showed definite correlation between the solubility of enamels and the milled enamel consistency and that factors other than Na_2O and B_2O_3 solubility must be taken into account.

In the present work, enamel compositions were selected with the objective of eliminating as many other variables as possible in order to study more thoroughly the effect of the Na_2O and B_2O_3 solubility variable.

II. Method of Investigation

(1) Selection of Compositions

A sheet-steel blue ground coat[2] was chosen as the basis for study. Both the total and the proportion of sodium and boric oxides were varied as shown in Fig. 1. In the actual formulation, these were calculated back to sodium carbonate and borax, all other materials being held constant. Enamel No. 4 is the basic composition. The batch compositions are shown in Table I.

This method of varying the compositions was chosen merely to simplify selection of compositions for the range of solubility desired.

(2) Milling

Duplicate millings were made of all compositions, using the following mill additions: 1500 grams frit, 105 grams Vallendar clay, and 550 to 600 grams distilled water.

The enamels were ground as nearly as possible to a fineness of 5 to 7 grams dry residue on a 200-mesh sieve from a 50-milliliter sample of liquid enamel taken from the mill. It was impossible to maintain the fineness within these limits in all cases because many of the enamels settled rapidly in the mill, thereby preventing accurate sampling before the mill was emptied. Some of the millings, though showing correct grinding when first sampled, were either slightly above or below the limits set when accurately sampled after the mill was emptied.

After milling, all enamels were adjusted to a specific gravity of 1.70.

(3) Consistency Measurements

Using the Gardner mobilometer,[3] consistency

Table I

	Enamel No. (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
B_2O_3	6.25	21.25	6.25	10.0	8.25	11.75	13.75	26.25	18.5	16	13.5	5	3.75	2.5	8.75	7	6	5
Na_2O	6.25	6.25	21.25	10.0	8.25	11.75	13.75	6.25	6.5	4	2.5	18.5	16.25	13.5	18.75	16.5	14	11.5
Total	12.5	27.5	27.5	20.0	16.5	23.5	27.5	32.5	25.0	20	16	23.5	20	16	27.5	23.5	20	16.5
Borax	17.1	38.3	17.1	27.3	22.6	32.1	37.6	38.6	40.1	24.7	15.4	13.6	10.3	6.8	23.8	19.1	16.4	13.7
Boric acid		12.8						21.5	6.4	12.4	14.1							
Soda ash	5.9		31.6	9.4	7.9	11.2	13.1					27.8	25.0	21.2	27.6	22.9	19.4	15.9

Basic Composition

Feldspar	32	Cobalt oxide	0.5
Quartz	20	Manganese dioxide	1.5
Soda niter	4	Borax	Variable
Fluorspar	5	Soda ash	"

* Presented at the Thirty-Ninth Annual Meeting, American Ceramic Society, New York, N. Y., March 23, 1937 (Enamel Division). Received February 18, 1937.

[1] G. H. McIntyre and R. E. Bevis, "Frit Solubility: I, Comparison of Methods of Determination and Relation of Soluble Salts to Enamel Slip Consistency," *Jour. Amer. Ceram. Soc.*, **19** [9] 249–52 (1936).

[2] A. I. Andrews, Enamels, p. 174. Twin City Publishing Co., Champaign, Ill., 1935.

[3] G. H. McIntyre and J. T. Irwin, "Application of Gardner Mobilometer to Enamel Slip Consistency Studies and Control," *Jour. Amer. Ceram. Soc.*, **15** [8] 433–38 (1932).

measurements were made of each milling, all measurements being made at 20° to 21°C.

A number of the enamels settled rather rapidly, but measurements were made possible by stirring the enamel thoroughly before allowing the plunger of the mobilometer to fall through it.

(4) Titrations, p_H Measurements

After consistency measurements were made, the enamel mill liquor was filtered off. Twenty-five milliliter samples were taken and diluted to 200 milliliters.

The p_H of these samples was determined potentiometrically, using a glass electrode.

The Na_2O titrations were made with 0.05 *N*HCl to an end-point of the methyl orange color change. Then the samples were boiled, Mannitol was added, and the B_2O_3 was titrated with 0.05 *N*NaOH to the color change of phenolphthalein.

III. Titration of Mill Liquor

A typical Na_2O titration is shown in Fig. 2.

In previous work, the authors' interpretation of the curve placed the end-point at p_H 7, the theoretical equivalence point for neutralization of a dilute strong base by a dilute strong acid. The slight leveling off of the curve between p_H 7 and p_H 6 followed by the slight inflection at p_H 5 was attributed to the buffering action of some unknown salt in solution.

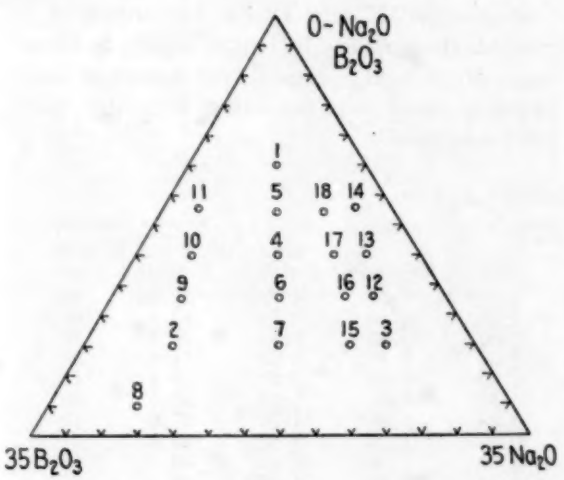

FIG. 1.

Further data have shown this interpretation to be partially incorrect. In Fig. 2, the titration curves of dilute solutions of borax, sodium carbonate, and a mixture of borax and sodium carbonate (10 to 1) are shown. The equivalence point of these solutions is at p_H 4.6 to 5 for all three curves. The curve of the borax-sodium carbonate mixture follows closely that of borax until

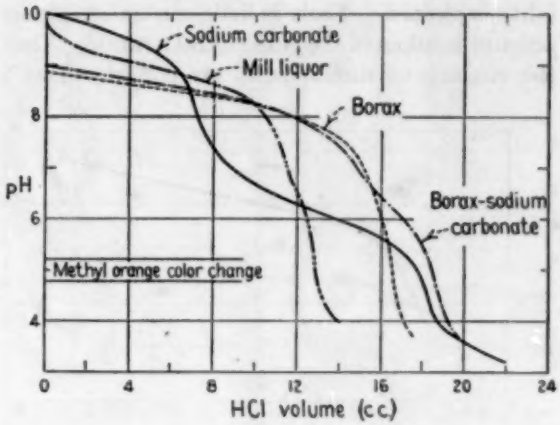

FIG. 2.

p_H 7 is reached. At this point, the small amount of sodium carbonate present begins to exert a buffering action, causing a slight leveling off of the curve until p_H 5.8 to 6 is reached, where both the borax inflection and the second inflection of sodium carbonate begin.

This curve duplicates almost exactly that of the enamel mill liquor. The leveling off of the mill-liquor curve between p_H 7 and 6 now can be explained by the buffering action of a small amount of sodium carbonate. In addition, this curve shows that there is no inflection at p_H 7, as the mill-liquor curve previously was interpreted, but rather at p_H 5.

This inflection takes place within the range of color change of methyl orange. It was found that the end-point as determined potentiometrically could be reproduced with reasonable accuracy using methyl orange indicator.

The potentiometric titration is more accurate than the indicator titration, but it was felt that the additional accuracy secured by the potentiometric titration was not consistent with the accuracy of other phases of the work. In addition, the time required for a potentiometric titration is much greater than that required for a titration using a chemical indicator. For these reasons, methyl orange was used as the end-point indicator in all titrations for Na_2O content.

IV. Results

The results are tabulated in Table II in the order of increasing Na_2O to B_2O_3 ratio.

(1) p_H Solubility Variable

In Fig. 3, the variation of p_H with total solubility is plotted. There is little correlation unless account is taken of the Na_2O to B_2O_3 ratio. When the enamels of similar ratio are considered as a

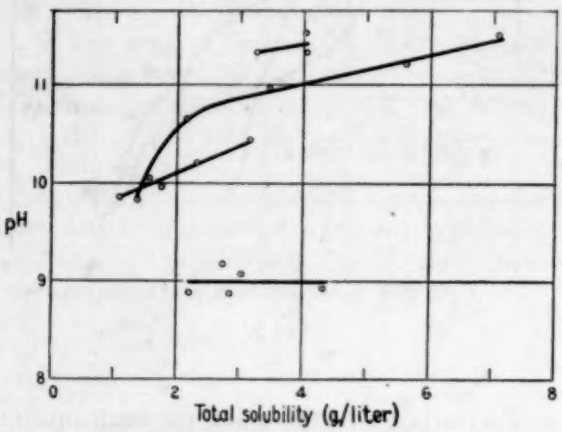

FIG. 3.—Hydrogen ion *vs.* total solubility.

group, a trend of increasing p_H with total solubility is shown. The ratio, however, seems to be more of a governing factor than total solubility.

In Fig. 4, the variation of p_H with Na_2O to B_2O_3 ratio is plotted. With increasing ratio, the p_H increases to a maximum of 11.5 at a ratio of 3.

Because of this correlation between p_H and ratio, any correlation shown between ratio and consistency will hold true to a large extent between p_H and consistency.

(2) Total Solubility and Enamel Consistency

The enamel compositions were grouped regardless of total solubility according to similar Na_2O to B_2O_3 ratios listed as follows (see also Table II):

Group I	Na_2O–B_2O_3 ratio
(No. 8)	0.28
Group II	
(Nos. 9, 10, 2, 11)	0.4–0.5
Group III	
(Nos. 5, 4, 1, 7, 6)	1.1
Group IV	
(Nos. 18, 17, 15, 3, 16)	2–3
Group V	
(Nos. 13, 14, 12)	6–8

In Fig. 5, total solubility of groups II, III, and IV is plotted against the corresponding relative mobility.

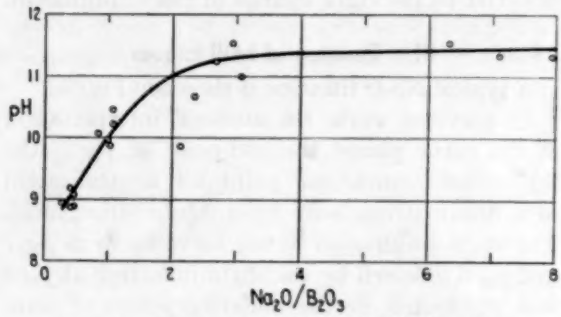

FIG. 4.—Hydrogen ion *vs.* Na_2O to B_2O_3 ratio.

In groups III and IV, as the solubility increased, the mobility increased rapidly to a maximum which held constant over a narrow range. Mobility again was decreased with still higher total solubility.

TABLE II

Group No.	Enamel No.	Slip characteristics	p_H	Mill liquor (g./liter) Na_2O	Mill liquor (g./liter) B_2O_3	Na_2O/B_2O_3	Total solubility	Relative consistency: Mobility	Relative consistency: Yield value
I	8	Good set	8.94	0.94	3.38	0.28	4.32	11.5	38
II	9	" "	9.18	0.80	1.95	0.41	2.75	15.0	36
	10	" "	8.88	0.84	2.02	0.42	2.86	29.5	30
	2	" "	9.08	0.97	2.07	0.47	3.04	14.6	26
	11	" "	8.89	0.72	1.49	0.48	2.21	19.5	73
III	5	Settles	10.06	0.72	0.85	0.85	1.57	35.5	20
	4	"	9.97	0.88	0.88	1.00	1.76	37.6	19
	1	"	9.87	0.56	0.54	1.04	1.10	22.6	21
	7	"	10.44	1.64	1.52	1.08	3.16	34.7	16
	6	"	10.21	1.21	1.11	1.09	2.32	39.5	17
IV	18	"	9.84	0.94	0.44	2.14	1.38	58.0	15
	17	"	10.65	1.51	0.64	2.36	2.15	72.0	15
	15	"	11.22	4.09	1.52	2.69	5.61	73.0	19
	3	"	11.52	5.28	1.79	2.96	7.07	43.0	13
	16	"	10.97	2.63	0.85	3.09	3.48	73.0	18
V	13	"	11.53	3.48	0.55	6.33	4.03	66.0	12
	14	"	11.33	2.85	0.40	7.13	3.25	62.5	15
	12	"	11.33	3.58	0.45	7.96	4.03	63.0	5

The enamels of group IV had a higher mobility as a whole and a longer range of maximum mobility.

The enamels of group II were confined to an area of low mobility, but no definite relationship could be determined. It is probable that in this range small changes in solubility made such a change in the consistency that the work was not sufficiently accurate to detect the relationship.

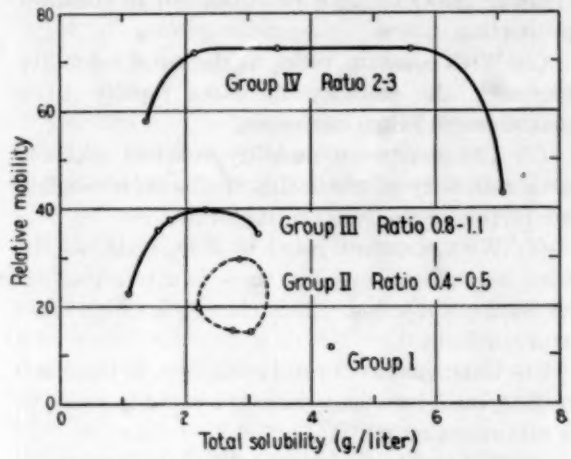

FIG. 5.—Relative mobility *vs.* total solubility.

Because group V contains only three compositions and covers only a small range of solubility, it was not plotted.

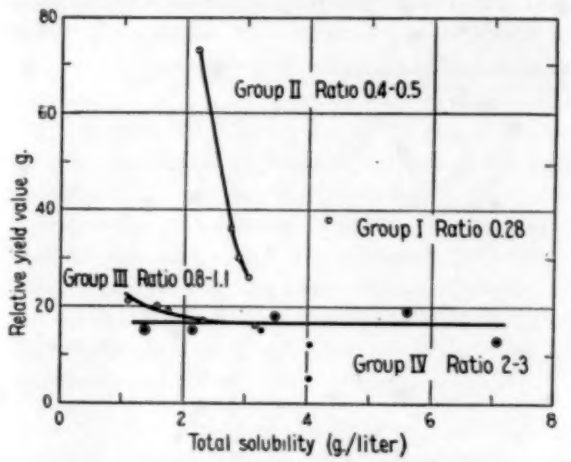

FIG. 6.—Yield value *vs.* total solubility.

In Fig. 6, the solubility is plotted against relative yield value. The enamels again are divided into groups of similar ratio.

In group II, there was a rapid decrease in yield value with increasing solubility; in groups III and IV, though there was a slight trend of decreasing yield value with increasing solubility, the change is hardly more than the experimental error. Again group V did not cover sufficient range to draw any conclusions.

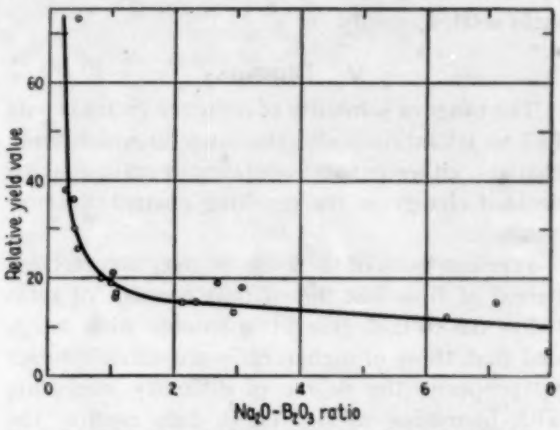

FIG. 7.—Relative yield value *vs.* Na_2O to B_2O_3 ratio.

(3) Na_2O to B_2O_3 Ratio and Enamel Consistency

The data of Table II show a trend of decreasing yield value with increase of ratio.

Figure 7 shows a close relationship independent of solubility between relative yield value and ratio. As the ratio increased, the yield value decreased rapidly to a minimum at a ratio of 1 with practically no further change even at very high Na_2O to B_2O_3 ratio.

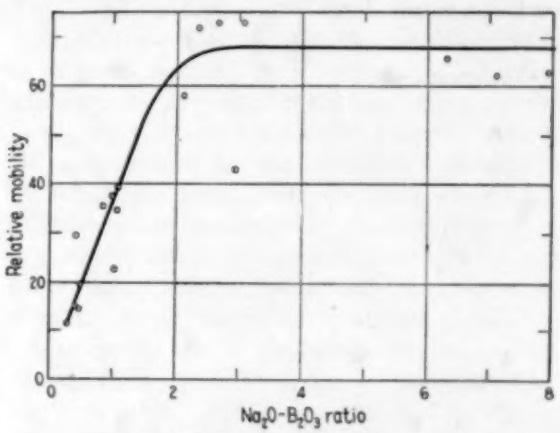

FIG. 8.—Relative mobility *vs.* Na_2O to B_2O_3 ratio.

It should be noted that enamel No. 11 is quite inconsistent. This point was checked by four millings with identical results. No explanation can be offered for this inconsistency.

In Fig. 8, the relative mobility is plotted against the ratio, independent of total solubility.

A close relationship is shown, the mobility increasing rapidly to a maximum mobility of 60 to 70 at a ratio of 1.5 to 2.5.

It is significant that all enamels of a ratio below 0.89 had good set and that those of a higher ratio settled rapidly.

V. Discussion

The range of solubility of ordinary ground coats (0.7 to 1.1 ratio) is also the range in which small changes, either in total solubility or ratio, make a decided change in the resulting enamel-slip consistency.

Previous work of the authors[4] over an extended period of time has shown that enamels of ratio below 0.8 to 0.85 give little trouble with setup, and that those of higher ratio are difficult to set up properly, the degree of difficulty increasing with increasing ratio. These data confirm the limiting ratio for settling and consistency factors as determined in the present work.

The ratio for an equimolecular solution of Na_2O and B_2O_3 is 0.89. It may be possible that this fact is connected in some way with this dividing line of good and poor set.

One application of these results would be to control enamel set by controlling the Na_2O to B_2O_3 ratio in the mill liquor by mill additions, but this may lead to other enameling difficulties. The authors plan to investigate this phase of the work at a future date.

[4] Unpublished data.

VI. Summary

These results show that for the same basic type of enamel there is definite correlation between the frit solubility and the resulting enamel slip consistency.

(1) The p_H of the mill liquor increases with increasing Na_2O to B_2O_3 ratio but not in constant proportion.

(2) With constant ratio, as the total solubility increases, the mobility increases rapidly to a maximum and then decreases.

(3) The maximum mobility reached and the total solubility at which this maximum is reached are factors of the Na_2O to B_2O_3 ratio.

(4) With constant Na_2O to B_2O_3 ratio, as the total solubility increases, there is a trend of decreasing yield value. This change is quite rapid at a low ratio.

(5) Independent of total solubility, as the Na_2O to B_2O_3 ratio increases, there is a rapid increase to a maximum mobility.

(6) Independent of total solubility, as the ratio increases, there is a rapid decrease to a minimum yield value.

(7) The most rapid changes in consistency take place in the range of solubility of common ground coats.

(8) The limiting ratio of Na_2O to B_2O_3 solubility for satisfactory enamel consistency appears to be that of equimolecular proportions of Na_2O to B_2O_3 or 0.89.

FERRO ENAMEL CORPORATION
4150 EAST FIFTY-SIXTH STREET
CLEVELAND, OHIO

LITHIUM MINERALS AND COMPOUNDS IN CERAMICS*

By George C. Betz

Abstract

A comparison of the chemical and physical properties of lithium and the more common alkali metals, sodium and potassium, is presented. The occurrence and chemical analyses of the commercial ores of lithium and the ceramic application of some of the lithium compounds are given.

I. Introduction

Lithium compounds have been of great importance in the development and growth of two of the newest engineering achievements, arc welding and air conditioning. Lithium compounds also play an important part in man's oldest art, ceramics.

Although lithium is of the alkali group, it differs in its chemical reactions from the other members of this family and resembles, in many respects, the members of the alkaline-earth group. This is particularly true of the reactions of certain lithium salts, such as the carbonate, fluoride, and phosphate which, unlike those of the alkali metals, are sparingly soluble in water.

Lithium is the lightest of all of the metals; it weighs less than one-fifth as much as metallic aluminum.

One pound of lithium is chemically equivalent to approximately 3.3 pounds of sodium or 5.5 pounds of potassium. It is for this reason that small percentages of lithium, when added to ceramic formulas, often exert powerful fluxing effects.

If the ores of lithium occurred in deposits that were as uniform and plentiful as the sodium- and potassium-bearing deposits, it is highly probable that the lithium minerals would be as extensively used in ceramics as are the feldspars. Unfortunately, this is not the case, although there are available large tonnages of sufficiently high-grade lithium-bearing ores, and they are being used in increasing quantities in the ceramic field.

II. Lithium Ores

Lithium has been found in more than one hundred and fifty different minerals, only three of which occur in sufficient quantity and contain a high enough percentage of lithium for consideration, *viz.*, amblygonite, spodumene, and lepidolite, all of which occur in pegmatite dikes.

Table I

Typical Analyses of Lithium Ores and Feldspar

	Amblygonite (%)	Spodumene (%)	Lepidolite (%)	Feldspar (%)
Li_2O	8.48	6.78	4.65	
K_2O	0.30	0.69	10.33	9.9
Na_2O	1.63	0.46	0.13	2.4
SiO_2	5.16	62.91	52.89	70.4
Al_2O_3	22.96	28.42	26.77	16.4
Fe_2O_3 or FeO	0.019	0.53	0.19	0.07
MgO	Tr.	0.13	0.31	Tr.
CaO	0.15	0.11	0.92	0.30
P_2O_5	54.42			
MnO_2	None		0.59	
F	2.67		3.68	
Loss on ignition	4.80	0.28	0.66	

Amblygonite is a complex lithium-aluminum fluophosphate, with the theoretical formula $Li(AlF)PO_4$, containing theoretically 10.1% of lithia. An actual chemical analysis of six carloads averaged 8.21% lithia with a minimum of 7.88% and a maximum of 8.59%.

Amblygonite, because of its high lithia content, is in great demand as a commercial source of lithium salts, and most of the available supply of amblygonite is utilized for this purpose. It can be recommended for use in ceramic formulas to produce rapid fluxing and high gloss, where phosphates are not detrimental. Its high percentage of fluorides and phosphates, together with its high lithia content, makes amblygonite especially effective as a fluxing ingredient in opaque glazes.

Spodumene is a lithium-aluminum silicate ($LiAl(SiO_3)_2$) which theoretically contains about 8.4% of lithia, 27.4% alumina, and 64.5% of silica. Commercial shipments usually contain from $4^1/_2$ to $7^1/_2$% lithia and average about 6%.

The available supply of spodumene is much greater than amblygonite and, for this reason, it is relatively lower in cost. Because the lithia content of spodumene is frequently leached out by weathering, it is often necessary to strip the exposed surfaces of the deposits to assure a satis-

* Presented at the Thirty-Ninth Annual Meeting, American Ceramic Society, New York, N. Y., March 23, 1937 (Materials and Equipment Division). Received April 13, 1937.

factorily high content of lithia. Chemical control of each shipment is recommended for all ceramic applications.

Spodumene, owing to its higher content of alumina, is relatively harder to melt than feldspar when added to a glass batch or body formula. For this reason, it has not been used extensively, even though its lithia and alumina content should make this mineral highly desirable. Spodumene is quite refractory; it has a relatively high melting point of approximately 2600°F as shown when substituted for feldspar in an electrical-porcelain formula.

	No. 1 feldspar body	No. 2 spodumene body
English ball clay	13	13
Florida kaolin	13	13
Georgia kaolin	15	15
Flint	26	26
Feldspar	33	
Spodumene		33

The mixtures were ball-ground in pebble mills for six hours with an excess of water. They were then filtered, and test specimens were prepared in the usual manner for dust-pressed electrical porcelain. Test specimens, 1 by 1 by 4 inches, were dust-pressed, dried, and fired to cone 11 down in a tunnel kiln.

The spodumene body formula No. 2 was highly porous and unexpectedly increased in size instead of shrinking in the firing process, whereas the feldspar body was vitrified and showed the characteristic firing shrinkage. There was no distortion from swelling or bloating in either body, the expansion of the spodumene body evidently being due to a uniform permanent expansion of the spodumene. The color of the spodumene body was buff compared to the white of the feldspar body.

	Water absorption (%)	Firing shrinkage (%) (dry sizes 100 %)	Firing expansion (%) (dry sizes 100 %)	Color
No. 1 feldspar body	1.23	8.85		White
No. 2 spodumene body	21.30		4.97	Buff

Although the color of this spodumene body is buff, samples of spodumene from other mines have been melted to clear colorless glasses at 2600°F. The expansion of lump spodumene was quite noticeable when heated rapidly in a crucible, and it was especially rapid just before melting took place.

(1) Beneficiation of Spodumene

The U. S. Bureau of Mines has recently published an interesting report on spodumene[1] which may lead to the commercial production of spodumene in a pure form at a relatively low cost. The "decrepitation" process depends for its success on the formation of a heat-inversion product different in crystal form from the natural spodumene, which can be separated from the associated minerals by mechanical processes. This altered crystalline form, which evidently is not found in nature, is referred to as "beta spodumene" in the Bureau of Mines publication to differentiate it from the natural spodumene crystal.

NOTE: Unfortunately the name, "beta spodumene," has already appeared in the literature to identify another mineral of a different chemical composition. Brush and Dana, *Amer. Jour. Sci.*, **20**, 257 (1880) refer to "beta spodumene" as an alteration product of spodumene, which consists of a mixture of albite and eucryptite ($LiAlSiO_4$) and contains 3.50% of lithia. Under the circumstances, it would seem desirable to differentiate between these two materials.

Experiments are now being conducted to determine the effect of substituting the calcined spodumene obtained by decrepitation for the natural uncalcined spodumene in ceramic formulas.

Spodumene, in finely divided form, has the effect of increasing the gloss of many high-temperature enamels. It is also being used to some extent as a source of lithia and alumina in special glasses.

Lepidolite, commonly called lithia mica, is a complex lithium-aluminum fluosilicate, $K \cdot Li(Al_2(OH \cdot F))Al(SiO_3)_2$ or $LiKAlF_2Si_3O_4$, with a theoretical lithium content of 6.4%. It varies considerably in chemical composition and lithia content, and careful mining supervision and chemical control of each lot of material is necessary to insure a uniform product suitable for ceramic consumption. It is usually sold on a guaranteed minimum content of 3% lithia for ceramic purposes. The average lithium content of seven recent shipments as received from the mines was 3.95% lithia.

Lepidolite exerts a very powerful fluxing action because of its high percentage of potash, lithia, and fluorine. When added in small amounts to ceramic bodies, it is an effective mineralizer which

[1]Foster Fraas and O. C. Ralston, "Beneficiation of Spodumene by Decrepitation," *Bur. Mines Rept. of Invest.*, No. 3336 (1937).

helps to promote rapid solution and subsequent recrystallization. It is particularly effective when added in small amounts to high talc and magnesia bodies.

Extensive use has been made of lepidolite in the manufacture of opal and special heat-resistant glasses. It is probably the most satisfactory and economical source of lithia for the glass industry, and it is available in sufficient quantity for large-scale commercial applications.

III. Lithium Salts

The presence of undesirable coloring impurities and the natural variation of the lithia content of the ores themselves have resulted in the substitution of chemically prepared lithium compounds, especially the technical grade of lithium carbonate for use in such ceramic products as optical glass, enamels, glazes, and glass colors. One pound of lithium carbonate will replace ten pounds of a 4%-bearing lithia ore. Where the actual cost of the raw material is secondary to absolute purity and uniformity, lithium carbonate is rapidly replacing lithium ores.

Lithium carbonate has many desirable physical properties. It melts more readily than sodium carbonate or potassium carbonate and forms eutectics with both of these compounds. The surface tension of molten lithium carbonate is lower than molten sodium or potassium carbonates. When used to replace lead oxide in a glaze or enamel, there is less tendency to vaporize and coat the kiln furniture with an undesirable glaze. This beneficial effect is especially noticeable above cone 2, and it has been used successfully to prevent the glazing of the inside of small, rapid-firing tunnel kilns in electrical porcelain production.

The addition of 1% of lithium carbonate to dinnerware, electrical porcelain, and sanitary-ware glazes has been found to increase the resulting gloss to a marked degree. In making this addition, however, it is necessary in some cases to adjust the glaze, inasmuch as the lithium carbonate produces a slight deflocculating effect.

Where fluorine is a constituent of the formula, lithium fluoride may be substituted for the carbonate, because the cost per pound of contained lithia is not much higher.

Application has recently been made for a patent covering the use of fused lithium nitrate for etching glass. When fused lithium nitrate comes into contact with a soda-lime glass at a temperature of 500°F or above for two to four minutes, a beautiful etching or frosting results that is comparable to the best fluoride etch.

Considerable experimental work has been done along this line, but no commercial application of this process has yet been made. Laboratory-scale operations, however, have been quite successful in several instances.

Lithium carbonate is the most economical and widely used of the lithium compounds in ceramics.

IV. Summary

The chief advantages to be gained by the introduction of lithia in ceramic formulas may be summarized as follows: (1) it produces powerful fluxing effects, especially in conjunction with feldspar; (2) it is a valuable constituent in certain glasses having low thermal expansion, because it permits the total alkali content to be kept at a minimum; (3) it enables the production of certain glasses having high electrical resistance and desirable working properties; (4) a high content of lithia enables the production of glasses that transmit ultra-violet light; (5) it acts as a powerful mineralizer in ceramic bodies; (6) when substituted for lead oxide, there is less tendency for the glaze to vaporize; and (7) it reduces the maturing temperature and greatly increases the fluidity and gloss of glazes and enamels.

As modern and efficient mining methods supplant the older and cruder operations and as new methods of concentrating are perfected and applied, it should be possible to produce lithium ores of high purity at a cost that should encourage a larger consumption.

Foote Mineral Company
1609 Summer Street
Philadelphia, Pennsylvania

GLASS INDUSTRY LEADERS PAY TRIBUTE

to

The American Ceramic Society

In the April, 1938, issue of *Glass Industry*, the editor and publisher, J. T. Ogden, reviews "Forty Years of the American Ceramic Society." The article appeared concurrently with the Fortieth Annual Meeting of the Society in New Orleans, March 27–April 2, 1938. Accompanying the *Glass Industry* article were statements of presidents of four of the country's large glass plants, in which they emphasized the value of the American Ceramic Society to the glass industry.

Corning Glass Works

Corning Glass Works sends heartiest congratulations to the American Ceramic Society on the occasion of its fortieth anniversary. The Society provides a worth-while forum for the discussion of technical problems related to ceramic industries, and Corning Glass Works wishes for it many years of continued activity and usefulness.

—AMORY HOUGHTON

Libbey-Owens-Ford Glass Company

The manufacture of glass started in this country in a small way. The road was not easy and many failures resulted, but perseverance won and the number of factories increased steadily. Technical information was either lacking or hard to secure. Contacts between glass men were few and far between. In the American Ceramic Society, however, an organization came into being, which aided in the exchange of information and published the results of extensive investigations which are invaluable to the glass technologist. Standard methods of testing glass and ceramic materials are being developed and improved; chemical analyses have become more reliable; educational facilities for glass technologists are improving; these and many more advances, I believe, can be attributed directly or indirectly to the influence of the American Ceramic Society.

Research, such as encouraged by the American Ceramic Society, has been an important factor in the progress made by the Libbey-Owens-Ford Glass Company; in fact, the Company was formed as the result of the successful completion of a major research problem—the production of sheet glass drawn in the form of a continuous ribbon from a tank furnace.

The Libbey-Owens-Ford Glass Company has continued to hold research in high esteem and as evidence of our faith in research, a new Technical Building will be completed with the next few weeks. This building, equipped with modern facilities for conducting research, will house the Chemical, Physical and Engineering Divisions of the Company; and problems pertaining to plastics, glass, refractories, and their production will be studied.

—JOHN D. BIGGERS

Owens-Illinois Glass Company

The Fortieth Annual Meeting of the American Ceramic Society being held this month recalls the great contribution it has made in the past through encouraging the utilization of ceramic technology in industry. The progress of this Society, particularly in recent years, is an indication of the even greater influence which it can exert in aiding the ceramic industries to make a more important place for themselves in the business of the future.

—WILLIAM E. LEVIS

Pittsburgh Plate Glass Company

The Pittsburgh Plate Glass Co., wishes to felicitate the American Ceramic Society on its fortieth anniversary. Starting modestly as most worth-while projects do, it has grown soundly to a mature institution of solid value. The fact that its growth and success depends entirely upon the unselfish coöperation of its members speaks impressively of its membership.

Our Company has recognized the value of research in glass and refractories, as evidenced by our research activities of the past four decades. This has been further emphasized by our recent expansion of those activities. One of the prime reasons for our past and present interest in research is our determination to provide the consumer market with the best products available in our field. Coupled with this is our equal determination of developing new products that will further enhance the well-being of humanity. The prosecution of these aims is definite evidence of a recognition of our obligations to mankind.

Individuals of our organization have given freely of their energies in service to the American Ceramic Society, and we feel that this contribution has been of mutual value. It is with sincerity that we hope the next half century will mark as much progress in the activities of the American Ceramic Society as the last forty years have shown.

—H. S. WHERRETT

CERAMIC ABSTRACTS

Compiled by the

AMERICAN CERAMIC SOCIETY

ROSS C. PURDY, Editor

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The bold-face number following the journal name is the volume; the issue number is in brackets, followed by the page numbers, then the year in parentheses.

May, 1938
17—5

Abrasives

Determination of size of fine abrasive powders. Comparative study of microprojection and sedimentation methods. FRANK L. JONES. *Ind. Eng. Chem., Anal. Ed.*, **10** [1] 45–47 (1938).—The determination of the particle size of fine abrasive powders by a microprojection method is described in detail. J. considers differences in size-distribution curves which were prepared for aluminum oxide abrasive powders using the conventional microprojection method and a common sedimentation method. The two methods are compared, and the advantages of each are discussed. F.G.H.

Finishing spindle carrier hole by grinding. FRED L. PRENTISS. *Iron Age*, **140** [20] 38–41 (1937).—The time of finishing holes has been reduced 500 to 600% by substituting boring for grinding. Closer tolerances and more accurate alignment are also obtained. Finish boring of drilled holes is done with a Carboloy-tipped tool. E. H. McC.

Grinding microscopic specimens on a lead disk with fixed abrasive. KURT AMBERG. *Jernkontorets Ann.*, **121**, 603–14 (1937); *Chem. Abs.*, **32**, 1062 (1938).—The lead disk is covered by a layer of varnish in which the abrasive is dispersed. The surface can be renewed by moistening with a soft brush dipped in benzene. Tungsten carbide powder is used for fine grinding. The method is suitable for difficult grindings such as the preparation of specimens for studying slag inclusions.

Grinding and polishing of synthetic materials. F. OHL. *Oberflächentech.*, **14** [18] 183–85 (1937).—O. describes polishing methods and agents, their manufacture, and fields of application for artificial plastic materials made of casein, albumen, hides, tar, cellulose, ketones, aldehydes, phenols, etc. M.H.

Investigation of the grinding process of corundum abrasives with a ceramic bond. Effect of the hardness of the disk. W. FRANTZ. *Werkstatt Betrieb*, **70**, 180–83 (1937); abstracted in *Chem. Zentr.*, **1937, ii**, 4372. M.V.C.

PATENTS

Abrasive article and manufacture thereof. NORTON GRINDING WHEEL CO., LTD. (Norton Co.). Brit. 479,703, 479,789, and 479,790, Feb. 23, 1938 (Dec. 15, 1936).

Abrasive article and method and apparatus for manufacturing. CARBORUNDUM CO. Brit. 479,767, Feb. 23, 1938 (Sept. 5, 1935).

Abrasive material. P. M. PAULSON (E. I. du Pont de Nemours & Co.). U. S. 2,111,272, March 15, 1938 (Aug. 18, 1936). A flexible abrasive article comprises a flexible base, abrasive grains, and a bond for securing the abrasive grains to the base, the bond comprising polyvinyl alcohol and an insolubilizing agent therefor.

Abrasive product and method of manufacturing. N. P. ROBIE (Carborundum Co.). U. S. 2,111,006, March 15, 1938 (Dec. 10, 1936). An abrasive article comprising abrasive grains and a solidified binder comprising a polymerized vinyl compound containing sufficient hydroxyl groups to be self-dispersible in water.

Abrasive wheel and mount therefor. H. S. INDGE (Norton Co.). U. S. 2,110,086, March 1, 1938 (June 25, 1935).

Abrasive wheels. DEUTSCHE NORTON-GES.M.B.H. Ger. 648,232, July 27, 1937; Cl. 80*b*. 11; *Chem. Abs.*, **31**, 7212 (1937).—An abrasive wheel comprises concentric zones of granular material united by binders of similar or identical composition, the zones being so composed that the inner zone has a higher mechanical strength than the outer zone, while both zones have about the same modulus of elasticity (within the ratio 1 : 2.6), coefficient of expan-

sion, and shrinkage characteristics. These results are obtained by using, in the inner zone, an abrasive of finer grain and (or) a higher proportion of binder and (or) a more easily vitrified ceramic binder. Examples are given.

Alumina and sodium hydroxide. S. P. KAMETSKIĬ AND P. F. KASHCHBEV. Russ. 42,993, May 31, 1935; *Chem. Abs.*, **31**, 7202 (1937).—Clay is first treated at 550° and then, together with $(NH_4)_2SO_4$, at about 400°. The product is treated with water and the solution treated with CaF_2 to form Al fluoride + sulfate; this is decomposed in the presence of NH_3 and water with the formation of alumina and NH_4F. The later is converted into NaF by means of NaCl and is then causticized with lime.

Apparatus for lapping. L. F. NENNINGER (Cincinnati Milling Machine Co.). U. S. 2,111,271, March 15, 1938 (July 12, 1935).

Blind end cylinder honing machine. F. A. SWANSON (Barnes Drill Co.). U. S. 2,108,354, Feb. 15, 1938 (June 8, 1935).

Buffing or polishing wheel. E. W. HALL. U. S. 2,108,966, Feb. 22, 1938 (Jan. 29, 1937).

Cam grinding device. C. J. GREEN (Norton Co.). U. S. 2,109,386, Feb. 22, 1938 (Nov. 17, 1937); continuation of application Serial No. 60,477 and 60,478, Jan. 23, 1936.

Cleaning and polishing block. J. J. KENNEDY (Chamberlain Co., Inc.). U. S. 2,108,405, Feb. 15, 1938 (Aug. 17, 1935). In a block of the character described, the block contains coarse aggregate pumice, fine natural pumice, magnesite, and one of a group comprising oxychloride cement and oxyphosphate cement.

Cutter sharpening machine. W. E. SYKES. U. S. 2,108,239, Feb. 15, 1938 (Feb. 8, 1934).

Dense nonmetallic bodies. J. A. BOYER AND C. G. ROSE (Carborundum Co.). U. S. 2,109,246, Feb. 22, 1938 (July 28, 1936).

Device for dressing grinding wheels with shouldered profile. FORTUNA-WERKE SPEZIALMASCHINENFABRIK AKT. GES. AND H. DANNER. Brit. 479,179, Feb. 16, 1938 (May 18, 1937).

Drill grinder. C. E. ADAMS. U. S. 2,109,308, Feb. 22, 1938 (March 3, 1936).

Fibrous buff. L. M. HAGUE (Hanson-Van Winkel-Munning Co.). U. S. 2,108,985, Feb. 22, 1938 (Dec. 2, 1936).

Finishing surfaces of gear teeth. BROWN & SONS (D. Huddersfield, Ltd., and H. E. Merritt). Brit. 480,247, March 2, 1938 (June 13, 1936).

Flexible-backed abradants. BRITISH THOMSON-HOUSTON CO., LTD. Brit. 479,820, Feb. 23, 1938 (May 16, 1936).

Gear lapping machine. E. R. NYLAND (General Motors Corp.). U. S. 2,108,547, Feb 15, 1938 (Feb. 13, 1935).

Grinding device. JOSEPH HRIBAR. U. S. 2,109,292, Feb. 22, 1938 (July 20, 1936). A grinding implement comprises an elongated frame equipped at its upper end with a crank-shaft bearing, a flexible endless belt of abrasive material mounted on a roller journalled in the frame, means for driving the belt, and means for adjusting the belt toward and away from the crank shaft.

Grinding device. A. W. WALKER (Carborundum Co.). U. S. 2,108,630, Feb. 15, 1938 (July 27, 1936). A grinding wheel comprises a homogeneous bonded abrasive disk, a rigid segmental framework embedded in one face of the disk.

Grinding instrument for use in dental work H. P. COUSSEMENT AND FLORIS CAPPETTE. U. S. 2,109,086, Feb. 22, 1938 (May 15, 1936).

Grinding machine. R. H. CRAMER (General Motors Corp.). U. S. 2,109,524, March 1, 1938 (Jan. 11, 1935). JONES & LAMSON MACHINE CO. Brit. 478,757, Feb. 9, 1938 (Oct. 25, 1935). C. H. KASCH (Micro-Westco, Inc.). U. S. 2,110,441, March 8, 1938 (Oct. 10, 1934). HERBERT VANDERBEEK (Timken Roller Bearing Co.). U. S. 2,109,600, March 1, 1938 (Oct. 5, 1934).

Grinding wheel mounting. H. W. H. BETH (Norton Co.). U. S. 2,110,619, March 8, 1938 (Jan. 4, 1936).

Hard carbide composition. J. A. BOYER AND C. G. ROSE (Carborundum Co.). U. S. 2,108,794, Feb. 22, 1938 (March 23, 1935). As a new manufacture, a fused carbide composition consists essentially of boron carbide and silicon carbide, in which silicon carbide is present as a separate crystalline phase which has solidified from a fused mass.

Hone. H. L. BLOOD (Heald Machine Co.). U. S. 2,110,756, March 8, 1938 (March 20, 1936).

Knitted buffing wheel. S. W. LIPPITT. U. S. 2,109,905, March 1, 1938 (Dec. 24, 1936).

Lapping machine. R. S. DRUMMOND. U. S. 2,111,045, March 15, 1938 (Aug. 7, 1935). A gear finishing machine frame.

Machine tool. H. I. DYER AND O. J. W. HEDLUND (Eaton Mfg. Co.). U. S. 2,110,931, March 15, 1938 (Oct. 23, 1935). In a machine tool, the combination of a magazine for supporting a plurality of articles and successively actuable to feed the articles to and away from a working position, chucking mechanism located at the working position and adapted to support an article in coöperative relation to a tool.

Machine tool for grinding and cutting metal. W. SPIERS, T. A. SPIERS, E. SPIERS, AND A. GHAYE. Brit. 478,755, Feb. 9, 1938 (Oct. 8, 1936).

Making composite abrasive article. A. L. BALL AND A. G. SCUTT (Carborundum Co.). U. S. 2,110,143, March 8, 1938 (March 23, 1935).

Manufacture of abrading or cutting tools of hard metal. F. EISNER. Brit. 480,157, March 2, 1938 (July 2, 1936).

Manufacture of covers for abrasive tools. FRANK NOWN (United Shoe Machinery Corp.). U. S. 2,110,937, March 15, 1938 (Jan. 15, 1937).

Manufacture of flexible abrasive article. R. C. BRYANT (Carborundum Co.). U. S. 2,108,645, Feb. 15, 1938 (March 18, 1933).

Means for sharpening drill. E. G. C. BARTON. Brit. 479,651, Feb. 23, 1938 (April 22, 1937).

Method of coating and apparatus therefor and product. E. C. SCHACHT (Behr-Manning Corp.). U. S. 20,660, Feb. 22, 1938 (Dec. 27, 1937); reissue of original U. S. 2,027,307, Jan. 7, 1936.

Polishing composition. L. W. SHUGER (Baltimore Paint and Color Works, Inc.). U. S. 2,108,214, Feb. 15, 1938 (March 12, 1936). An emulsion polishing composition highly resistant to weather ravages comprising, as a luster restorer, an odorless stearine-free fish oil and, as a lubri-

cator and cleanser, mineral oil and water, and in which the water is the continuous phase.

Polishing wheel. S. W. LIPPITT. U. S. 2,109,906, March 1, 1938 (Dec. 24, 1936).

Portable surface grinding machine. E. G. MOFFETT. U. S. 2,109,827, March 1, 1938 (May 12, 1937).

Producing hard cemented carbide composites. G. J. COMSTOCK. U. S. 2,108,797, Feb. 22, 1938 (Jan. 22, 1935). In the sintering process for producing articles of razor-edge sharpness, the steps of controlling the hardness of the presintered composite comprise mixing hard metal carbides with a cementing metal in powdered form, applying a pressure of more than 60,000 lb./sq. in. to the composite, applying a controlled presintering temperature just short of the final sintering temperature and varying in accordance with the hardness desired, working the composite to form fine-edge blades, and thereafter applying a final sintering temperature.

Roll grinding machine. H. J. GRIFFING (Norton Co.). U. S. 2,108,310, Feb. 15, 1938 (Dec. 20, 1935).

Sanding machine. T. F. BRACKETT (General Motors Corp.). U. S. 2,108,193, Feb. 15, 1938 (Oct. 30, 1936).

Sanding and polishing machine. C. J. LIPPOLD (J. M. Nash Co.). U. S. 2,109,069, Feb. 22, 1938 (June 24, 1935).

Shellac-bonded abrasive article. R. H. MARTIN (Norton Co.). U. S. 2,110,630, March 8, 1938 (Nov. 25, 1935). An abrasive wheel comprises a body of abrasive grains united by a bond of shellac containing an insoluble fluoride incorporated directly therein which is capable of and proportioned for giving greater stiffness to the shellac bond and causes cooler grinding under normal and otherwise constant conditions.

Table surfacer. R. C. MUZZO. U. S. 2,111,052, March 15, 1938 (April 9, 1936).

Tool carriers for boring, grinding, and like machine tools. A. H. STEVENS (Leland Electric Co.). Brit. 480,317, March 2, 1938 (Aug. 17, 1936).

Ventilated buffing wheel. HARRY ZIMMERMAN. U. S. 2,110,494, March 8, 1938 (Feb. 16, 1937).

Art and Archeology

Collections of old glass and ceramic work in Würzburg. RUDOLF SCHMIDT. *Glastech. Ber.*, **15** [12] 465–67 (1937). J.F.H.

Evaluating work, especially glass art work. W. WAGENFELD. *Glastech. Ber.*, **15** [5] 173–77 (1937). J.F.H.

Exhibition of stained glass. HELEN COMSTOCK. *Connoisseur*, **101** [438] 94–96 (1938).—The Van Baarn galleries were opened with an exhibition of stained and painted glass from the 12th Century to the close of the 16th Century. Twenty-seven panels, mostly of French origin, represented the evolution of ecclesiastical and secular glass in Europe. While the range of color in glass was much greater after the discovery of oxide stains and translucent enamels, the glass of the 12th and 13th centuries is rich in effects gained by the variation of a single tone, achieved by the use of uneven thickness for the small pieces of glass. M.E.P.

Form and decorativeness of glass from the viewpoint of hand or industrial production. W. LOTZ. *Glastech. Ber.*, **15** [10] 384–89 (1937). J.F.H.

Glassware. ANON. *Design*, **39** [8] 25 (1938).—Early American glass bottles, enameled tumblers and a flask from the factory of Baron Stiegel, three early Ohio blown-glass bottles, and two pieces of molded Stiegel glass are illustrated. M.E.P.

"Lion" jewel: a work of Corvinianus Saur in the possession of Lord Fairhaven. CHARLES R. BEARD. *Connoisseur*, **101** [438] 72–75 (1938).—B. describes the richly splendid Renaissance "Lion" jewel which shows on the reverse side of its setting the technique of translucent enamels on gold as known and used by Corvinianus Saur, court goldsmith to King Christian IV of Denmark, in the years 1591 to 1597. Illustrated. M.E.P.

Nal pottery. N. G. MAJUMDAR. *Proc. Indian Sci. Congr., 25th Congr.*, **1938**, Part 3, pp. 195–96.—In 1903 a number of polychrome vases bearing geometric patterns were discovered in the Sohr Damb mound at Nal in the Kalat State of Baluchistan and subsequently sent to the McMahon Museum at Quetta. An account of it by John Marshall was published in *Archaeological Survey of India, Ann. Rept.*, 1904–1905. In 1925 a systematic exploration of the site resulted in the discovery of prehistoric burials, and from them were recovered further examples of the same polychrome pottery. Since then it has received further attention from scholars in connection with the discoveries at Mohenjo-daro and other sites of the Indus valley. During M.'s exploration in Western Sind in 1929–30 and 1930–31, polychrome vases with geometric patterns, which recall to some extent the Nal examples, were excavated at a number of sites. This has necessitated a fresh study of the Nal pottery. A major part of the Quetta collection has been transferred to the Indian Museum, Calcutta. M. attempts tentatively to indicate the position in order of sequence of this pottery and of the kindred ware from Sind and Baluchistan. Further excavations and researches in this terrain are suggested to obtain a more definite idea of their sequence. A.P.S.

Newcomb Art School. ANON. *Bull. Amer. Ceram. Soc.*, **17** [3] 121 (1938).

Pottery: Czechoslovakia. ANON. *Design*, **39** [7] 24–25 (1938).—The earliest Czechoslovak ware known is earthen vessels and fired tile glazed with simple transparent lead glazes. The enamel-painted ceramics probably were not known until the 16th Century under the influence of the Italian Renaissance when majolica was introduced. The Haban pottery of that time was named after a troup of Anabaptists who were exiled from Germany. The Sobotiste ware was famous for a bluish white glaze and good forms. The glaze used in the second half of the 19th Century was yellow-gold. Slovak majolica is rare because of its rich colors and its technical perfection. See *Ceram. Abs.*, **12** [4] 165 (1933). M.E.P.

Pottery development work in Mexico. B. W. THORNGATE. *Bull. Amer. Ceram. Soc.*, **17** [3] 157–58 (1938).

Realization of the efforts of the technical group, "glass art work." B. KINDT. *Glastech. Ber.*, **15** [5] 177–83 (1937). J.F.H.

Samian ware (terra sigillata). M. V. TAYLOR. *Antiq-*

uity, **12**, 103 (1938).—F. O. Waage's protest against the misuse of the word "Samian" (*ibid.*, **11**, 46 (1937)) is timely. The ware made in Gaul should be known as Gaulish varnished ware or Romano-Gaulish varnished ware. The term "sigillata" should not be used for pottery which is not stamped. A.B.S.

Selenium pink as a glass color and its modification by rare earths. J. LÖFFLER. *Glastech. Ber.*, **15** [10] 389–93 (1937).—The cullet-batch ratio must be kept constant to produce uniform selenium colors. The correct degree of oxidation must be determined with the proper melting conditions, including cullet-batch ratio. The use of cerium oxide makes possible any degree of oxidation without after effects on the color. Cerium oxide containing neodymium is preferred, since small amounts of the latter cover up brownish tints, strengthen the color, and shift it toward a purer red. Saltpeter should chiefly be used for fining, using 1 to not more than 5 kg./100 kg. sand. Some sulfate can be used advantageously but should be kept down usually to 200 to 500 g./100 kg. sand. Boric acid can be used satisfactorily to soften a selenium glass. J.F.H.

Tulip ware. ANON. *Design*, **39** [8] 12 (1938).—The art of pottery making which the Pennsylvania Germans continued when they settled here produced a great variety of ware because the potteries were small and isolated. The two main types of ware, common and presentational, were made of simple materials. Common red-firing clay was used for the body, and cream-colored clay thinned with water was used for the slip. The glaze was composed of a mixture of clay and red lead or galena. For elaborate pieces, the glaze was colored with copper and manganese. A complete list and description of the primitive implements used are given. To prevent any unevenness on the surface of the flatware, the slip decoration was traced on the clay disk and pounded with the "batter" before molding. Illustrated. See *Ceram. Abs.*, **11** [7] 399 (1932); "De Forest—," *ibid.*, **14** [2] 29 (1935). M.E.P.

PATENTS

Coating pottery. SCHÜTTE A.-G. FÜR TONINDUSTRIE (Theodor Schumann, inventor). Ger. 650,375, Sept. 20, 1937; Cl. 80*b*. 23.03; *Chem. Abs.*, **32**, 1066 (1938). Addition to Ger. 626,112 (*Ceram. Abs.*, **15** [8] 249 (1936)).—Coatings having a terra sigillata appearance are produced on pottery by a modification of the process of Ger. 626,112, in which, in place of a peptized clay sludge having a specific gravity of 1.2 or less, use is made of a peptized clay sludge having an initial viscosity of about 10 centipoises or less. The sludge is allowed to stand for about 24 hr., decanted, and then applied as described in Ger. 626,112, a relatively low firing temperature (about 600°) being used until chemically combined water has been removed.

Decorative enamel. MIGEOT FRÈRES. Fr. 813,737, June 8, 1937; *Chem. Abs.*, **32**, 1068 (1938).—Powder or flakes of mica, nacre, or other brilliant products infusible at the softening temperature of the enamel are added to ename to give a decorative effect.

Designs for:

Bottle. G. M. CLEVENGER (Maryland Glass Corp.). U. S. 108,778, March 15, 1938 (Jan. 20, 1938). E. W. FUERST (National Distillers Products Corp.). U. S. 108,593, Feb. 22, 1938 (Dec. 13, 1937). W. R. KOHL. U. S. 108,449, Feb. 15, 1938 (July 10, 1937). P. G. LLOYD (Carr-Lowrey Glass Co.). U. S. 108,451, Feb. 15, 1938 (Aug. 3, 1937). F. J. PETTY (Ball Bros. Co.). U. S. 108,795, March 15, 1938 (Sept. 16, 1937). F. J. PETTY (Godefroy Mfg. Co.). U. S. 108,796, March 15, 1938 (Jan. 20, 1938).

Building block. F. E. POORTINGA (Redfield Brick & Tile Co.). U. S. 108,455, Feb. 15, 1938 (Dec. 27, 1937).

Glass. M. O. HANSEN (Libbey Glass Co.). U. S. 108,746, March 8, 1938 (July 17, 1937).

Glass jar. R. H. DALLAS (Glass Containers, Inc.). U. S. 108,592, Feb. 22, 1938 (Dec. 27, 1937).

Goblet. R. R. KOSTELLOW (United States Glass Co.). U. S. 108,698, 108,699, and 108,748, March 8, 1938 (Jan. 22, 1938). U. S. 108,700, March 8, 1938 (Jan. 28, 1938). U. S. 108,787, March 15, 1938 (Jan. 28, 1938). U. S. 108,790, March 15, 1938 (Jan. 29, 1938).

Jar. W. L. KENNEDY (Crosse and Blackwell Co.). U. S. 108,594, Feb. 22, 1938 (Jan. 13, 1938).

Jug. LORENZO CELLA (Roma Wine Co., Inc.). U. S. 108,591, Feb. 22, 1938 (Dec. 28, 1937).

Mixing bowl. A. E. HULL. U. S. 108,445, Feb. 15, 1938 (Nov. 4, 1937).

Plate. R. R. KOSTELLOW (United States Glass Co.). U. S. 108,789, March 15, 1938 (Jan. 28, 1938).

Relish tray. R. A. KELLY (United States Glass Co.). U. S. 108,447, Feb. 15, 1938 (Nov. 11, 1937).

Stemmed goblet. ELMER BELL (Bryce Bros. Co.). U. S. 108,557, Feb. 22, 1938 (Jan. 17, 1938). U. S. 108,741, March 8, 1938 (Feb. 1, 1938).

Tray. R. A. KELLY (United States Glass Co.). U. S. 108,448, Feb. 15, 1938 (Dec. 2, 1937).

Tumbler. R. R. KOSTELLOW (United States Glass Co.). U. S. 108,788, March 15, 1938 (Jan. 28, 1938).

Screen stencil and method of making. W. D. BELL (Solar Laboratories). U. S. 2,110,319, March 8, 1938 (July 22, 1935).

Cements

Chemical constitution of Portland cement and development of its technical properties. Introduction to the study of special cements. MICHEL J. M. JASPERS. *Rev. Matériaux Construction Trav. Publics*, No. 327, pp. 273–77 (1936); No. 328, pp. 10–13; No. 329, pp. 29–32; No. 330, pp. 58–60; No. 331, pp. 82–84; No. 332, pp. 98–104; No. 333, pp. 126–31; No. 334, pp. 146–52 (1937); see *Ceram. Abs.*, **16** [3] 82 (1937). M.V.C.

Colored Portland cements. M. YA. BYCHKOV AND K. S. ZATZEPIN. *Tsement*, **5** [8] 27–32 (1937).—An addition of chrome oxide to the white cement mixture forms, on firing, a green silicate mineral which has higher refractive properties than ordinary clinker minerals. Positive results are obtained by replacing the oxide with $K_2Cr_2O_7$ and K_2CrO_4. The cement obtained is of a good quality and of standard properties. P.B. & E.S.

Determination of degree of hydration of cements. ANTONI EIGER. *Rev. Matériaux Construction Trav. Publics*, No. 335, pp. 161–65; No. 336, pp. 187–92 (1937).—E. found that all data, *e.g.*, cement quality, time of hardening, and quantity by unit of volume, may be replaced by one "quasi universal" characteristic for all Portland cements, that of the degree of hydration; this is equivalent in practice to the quantity of hydrosiliceous gel developed under the conditions given. A literature index is included. M.V.C.

Investigations on celite: IV–VII. YOSHIAKI SANADA. *Jour. Soc. Chem. Ind. Japan*, **40** [11] 395B; [12] 461–62B (1937); **41** [1] 8–9B (1938).—The effect of iron modulus on clinkering of the raw mix and the testing of cements with an iron modulus of 0.3 to 0.5 are discussed. For Parts II–III see *Ceram. Abs.*, **16** [5] 143 (1937). M.V.C.

Magnesia of Portland cement: III–VII. Y. SANADA. *Jour. Soc. Chem. Ind. Japan*, **40** [7] 244–46B; [11] 396–97B; [12] 460–61B (1937); **41** [1] 10B (1938).—The synthesis of $MgO \cdot SiO_2$ and $2MgO \cdot SiO_2$ and the effect of magnesia on the synthesis of calcium silicates were studied. For Part II see *Ceram. Abs.*, **16** [6] 167 (1937). M.V.C.

Minor constituents in Portland cement clinker. HERBERT INSLEY AND HOWARD F. MCMURDIE. *Jour. Research Nat. Bur. Standards*, **20** [2] 173–84 (1938); R.P. 1074. Price 10¢.—The optical and structural properties of some minor phases in Portland cement clinker, as observed in thin sections, polished sections, and a new type of polished thin section, are recorded. The similarity of such phases to those found in laboratory preparations is pointed out. Methods of determination of free CaO, free MgO, "light" interstitial material, and "dark" interstitial material are given. The "light" interstitial material is shown to be $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$. There are three kinds of "dark" interstitial material which have properties of (1) glass, (2) $3CaO \cdot Al_2O_3$, and (3) a prismatic crystalline material. The prismatic crystalline material apparently is a compound of the alkalis with some of the other oxides in the clinker. Glass is found in the majority of Portland cement clinkers. At present it is impossible to calculate precisely the compound composition from chemical analyses because of the lack of knowledge of cooling conditions, the effect of minor constituents on phase relations, and other variables. R.A.H.

BULLETIN

Effect of Na_2O, CaO, and MgO on ash fusion temperature using synthetic coal ash. THOMAS ESTEP, HARRY SELTZ, AND WILLARD J. OSBORN. *Carnegie Inst. Tech., Coöp. Bull., Mining & Met. Invest.*, No. 74, 14 pp. (1937). Price 25¢.—Synthetic ash was made from kaolin and pure forms of SiO_2, Fe_2O_3, $CaSO_4$ or $CaCO_3$, and Na_2CO_3. Of 18 ashes studied, the natural and synthetic ash fusion temperatures checked within 51 °F in 15 cases. A satisfactory correlation of ash fusion temperature and composition was established by considering the ash as a four-component system of Al_2O_3, SiO_2, Fe_2O_3, and CaO. The effect of MgO was identical with that of CaO up to 10% and can be summed with the CaO. To correct for alkali present, the fusion temperature should be reduced 50 °F for each percentage of Na_2O present. The CaO fusion temperature relation is practically linear up to 5% with a 50 °F decrease for each percentage of CaO; the behavior was found to be irregular above 5%. B.C.R.

PATENTS

Cement manufacture. MIKAEL VOGEL-JORGENSEN (F. L. Smidth & Co.). Can. 371,674, Feb. 1, 1938 (Sept. 3, 1936). G.M.H.

Cement manufacture. MIKAEL VOGEL-JORGENSEN (F. L. Smidth & Co.). U. S. 2,111,517, March 15, 1938 (Sept. 3, 1936). A method of producing slurry for use in cement manufacture comprises adding a foam-generating substance to a mixture of cement raw materials and water and agitating the mixture until it is converted into foam.

Cement production. OLE ROLFSEN. Can. 371,739, Feb. 1, 1938 (Feb. 26, 1937). G.M.H.

Gypsum composition. T. P. CAMP (Canadian Gypsum Co., Ltd.). Can. 371,292, Jan. 18, 1938 (May 28, 1937; in U. S., June 20, 1936). G.M.H.

Magnesium oxychloride production. FRITZ WIENERT (Magnesium Elektron, Ltd.). Can. 371,478, Jan. 25, 1938 (Dec. 18, 1936). G.M.H.

Enamel

Acid-stable and nonpoisonous enamel. C. A. OTTERSBACH. *Glashütte*, **67** [4] 647–49 (1937).—The most suitable raw materials for the production of acid-stable and nonpoisonous enamels are cryolite, fluorspar, and quartz, calcite (up to 30%), magnesium carbonate, clay (up to 10%), etc. Cerous oxide is recommended as opacifier. Hair cracks in acid-stable enamels are avoided when the melting point of the ground coat is higher than that of the coat enamel by at least 50°. M.V.C.

Acid-stable enamel. VIELHABER. *Emailwaren-Ind.*, **14** [41–42] 28–789 (1937).—In answer to the paper of Ottersbach (see preceding abstract), V. maintains that the extent of the acid attack on an enamel depends on the ratio of refractory constituents (feldspar and quartz) to that of fluxes (borax and soda). The ratio of feldspar + quartz to that of borax must be larger than 2; a value of 3 is better. See *Ceram. Abs.*, **16** [8] 235 (1937). M.V.C.

Attack of water on enamels. VIELHABER. *Emailwaren-Ind.*, **14** [47] 323–24 (1937).—Experiments showed that water slowly dissolved the borax content and, to a lesser degree, the soda content of the enamel. Borax is not a suitable material for acid-stable enamels and should be partially replaced by soda. M.V.C.

Borosilicate frit for enamel. WALTER OBST. *Emailwaren-Ind.*, **14** [49] 337–38 (1937).—O. discusses present-day literature on the effect of borax in enamels. A patent of Nölling (Ger. 653,230), in which the borax or boric acid content of the enamel is partly or completely replaced by a strontium-calcium-magnesium-borosilicate, is analyzed. M.V.C.

Calculation of the coefficient of expansion of enamels.

VIELHABER. *Emailwaren-Ind.*, **14** [50] 345–46 (1937).—Difficulties encountered in the calculation of the coefficient of expansion of enamels are discussed. Tables showing the calculated and actual values are given. M.V.C.

Chemistry of silica. VIELHABER. *Emailwaren-Ind.*, **14** [50] 348–49 (1937).—The types of silica used in the enamel industry, silica compounds, and their formation are briefly discussed. See "Silica," *Ceram. Abs.*, **16** [3] 98 (1937). M.V.C.

Chilling enamel. VIELHABER. *Emailwaren-Ind.*, **14** [46] 316–17 (1938).—When enamel is melted in a tank furnace, difficulties are encountered in chilling it. Methods used at present are briefly dealt with. M.V.C.

Cleaning metallic surfaces. C. B. F. YOUNG. *Iron Age*, **140** [16] 185–88, 190, 192, 194–200; [17] 40–43 (1937).—Y. classifies and briefly describes various methods and gives a survey of the methods and advantages of sand-blasting and tumbling. See "Metal—," *Ceram. Abs.*, **16** [11] 330 (1937). E.H.McC.

Coat glazes. VIELHABER. *Emailwaren-Ind.*, **14** [50] 346–48 (1937).—Coat glazes (1) must be weather-stable, (2) must have the highest possible luster, (3) can not be difficult to melt, (4) must not affect colors, and (5) must not be opaque. Several batches are analyzed. To obtain blue color tones, from 0.1 to 0.2% cobalt oxide may be added. M.V.C.

Control of pickling bath. VIELHABER. *Beizerei* (in *Emailwaren-Ind.*, **14** [47]), **2** [11] 42–44 (1937).—Methods of keeping the pickling bath warm and of analyzing the concentration of pickling and neutralizing baths are discussed. M.V.C.

Effect of boiling acids on enamels. VIELHABER. *Emailwaren-Ind.*, **14** [41–42] 285–86 (1937).—V. discusses various methods used to determine acid stability of enamels, with special emphasis on the experiments of E. E. Bryant (*Jour. Amer. Ceram. Soc.*, **20** [10] 317–19 (1937)). M.V.C.

Enameling copper ware. VIELHABER. *Emailwaren-Ind.*, **14** [43] 298–99 (1937).—The enameling of ornamental or artistic copper ware is described. The ware has etched or engraved designs which are filled up with the so-called cell enamel. Transparent or opaque enamels adhere to copper only when their expansion is adapted to that of copper. White enamels for sheet iron can usually be used without ground enamel. Not all enamels melt at the same temperature; black and blue enamels are usually more easily melted than green and red enamels. M.V.C.

Grain size of raw materials. VIELHABER. *Emailwaren-Ind.*, **14** [44–45] 304–305 (1937).—Quartz may be ground coarser (0.12 to 0.14 mm.) for ground enamels but much finer (0.05 to 0.09 mm.) for coat enamels. Feldspar with a grain size of 0.12 mm. diameter has the highest melting rate; the grain size of calcite may be 0.43 mm. because of the dissociation of carbonate which promotes a more rapid reaction. M.V.C.

Grinding enamel. VIELHABER. *Emailwaren-Ind.*, **14** [34] 237–38 (1937).—V. discusses factors affecting the grinding of enamel, such as duration, temperature, raw materials, etc., and their effect on enamels. See *Ceram. Abs.*, **16** [5] 144 (1937). M.V.C.

Improving damaged enamel coats. ALDINGER. *Glashütte*, **67** [46] 710–11 (1937).—The damaged places in the enamel coat are cleaned and the same kind of enamel powder is sprayed over it by compressed air; the enamel powder is simultaneously heated. Hard enamel lacquer can be applied on the damaged places. Special cement with a water-glass base can also be used. M.V.C.

Installation for cleansing sheet iron. OTTO VOGEL. *Beizerei* (in *Emailwaren-Ind.*, **13** [35]), **1** [2] 6–7 (1936).—Details of construction of a special washing machine for cleansing sheet iron are given. M.V.C.

Metal deposition in arc welding. G. E. DOAN. *Welding Jour.* [N. Y.], **17** [1] Supp. 15–19 (1938).—D. describes fundamental research in which a study of the drop formation on the end of the metal electrode has been paralleled with the drop formation of liquids at the end of the capillary tube. Results and mathematics indicate that a reduction of surface tension of molten steel in the arc would reduce drop size and increase the melting rate and efficiency of the welding current. Additions of various metals were made to the electrode coating, the most successful addition and method being metal spray of Sb directly to the bare rod surface. Oscillograms show greater drop frequency and less short circuiting with this method. W.H.B.

Mill additions containing oxides. VIELHABER. *Emailwaren-Ind.*, **14** [41–42] 286–87 (1937).—V. discourages the addition of metallic oxides to the mill but recommends adding them directly to the enamel melt to improve adherence of the enamel to iron. M.V.C.

Quartz and feldspar in ground enamel. VIELHABER. *Emailwaren-Ind.*, **14** [48] 330–31 (1937).—Enamel with a low silica content is easily fused and therefore feldspar is added. It is not advisable, however, to add too much feldspar because it affects the elasticity of the enamel. M.V.C.

Report of the Subcommittee on Welding of Low Alloy Steels. J. H. CRITCHETT. *Welding Jour.* [N. Y.], **17** [1] 22–26 (1938).—S. makes a thorough survey of all the low carbon balanced alloy steels in regard to analyses and welding characteristics. Three general classifications of welding are made: (1) foolproof steels easy to weld and containing, in general, 0.15% C or less; (2) intermediate weldability steels containing less than 0.30% C, having a large enough drop in ductility in the heat-affected area to require stress relief or other heat treatment, and requiring special attention when fillet welded; and (3) difficultly weldable, "tricky" steels with more than 0.30% C and for which heat treatment subsequent to welding is essential. C. tabulates the data, indicating the physical properties and impact value to be expected for the steels under the conditions of welding and testing as stated. The classification of weldability is based on hardenability which is considered by the committee as a very rough qualitative index of ductility and may be highly misleading. W.H.B.

Sheet-steel ground-coat enamels. R. M. KING. Presented at meeting of Institute of Vitreous Enamellers, London; *Ohio State Univ. Eng. Expt. Sta. News*, **9**, 9–11 (April, 1937); *Sheet Metal Ind.*, **11** [122] 557–58 (1937).—A theoretical study of the rôle of cobalt oxide as an adherence-promoting agent in present-day commercial sheet-steel ground coats is given. K. deplores lack of a satisfactory method for determining the numerical value of

adherence and sums up the special case of cobalt-bearing ground coats as follows: (1) iron oxides and metallic iron are precipitated at the interface; (2) adherence is associated with precipitated metal in all cases but not always with precipitated oxides; (3) roughness of surface or differential etching are not important factors in adherence; and (4) coefficient of expansion is not a direct factor in adherence. Experiments showed that tungstic oxide, molybdic oxide, and antimony trioxide, when incorporated in a ground-coat base, would produce a satisfactory white ground coat for sheet steel, the ideal of all enamelers. Facts established regarding "reboiling," another ground-coat problem, are as follows: (1) it is peculiar to ground coats containing nickel and cobalt oxides when applied to steel; (2) if the ground coat is fired *in vacuo* by a special procedure, reboiling will not take place on subsequent heating; and (3) it apparently takes place when metallic precipitates are formed at the interface. Hence, reboiling, metallic precipitation, and adherence are apparently related. **Discussion.** A. L. EDWARDS. *Ibid.*, [122] 558 (1937).—The discussion showed a dissimilarity between the practical and the highly theoretical viewpoints. A.P.S.

Shrinkage stresses in welding. Review of literature to January 1, 1937. W. SPRAGEN AND G. E. CLAUSSEN. *Welding Jour.* [N. Y.], **16** [11] Supp. 2–62 (1937).—A comprehensive digest of the work in this field is given with conclusions as to the amount of stress, distribution with various welding methods, and an evaluation of the methods used by various investigators. A bibliography of 160 references is appended together with notes on methods of measuring strain. Suggested research problems on shrinkage stresses are listed. W.H.B.

Sorting enamel according to color tone. VIELHABER. *Emailwaren-Ind.*, **14** [25] 177–78 (1937).—Factors influencing the color tone of enamels are (1) fineness of grinding, (2) thickness of the coat, (3) firing temperature, (4) firing time, and (5) thickness of the ware to be enameled. Illumination of the room is of the greatest importance for the appearance of the color tone. The strength of light, whether sunlight or artificial, and the time of comparison (morning or evening) are factors which make the sorting of enamel by color tone extremely difficult. M.V.C.

Structure of enamels. R. ALDINGER. *Keram. Rundschau*, **45** [22] 237–39 (1937).—It is possible to find an enamel for any given use but there is no enamel fit for all purposes. For sheet ground coat, adherence is essential; cobalt oxide is better than nickel oxide. The fusibility must be adapted to the thickness of the sheet and the fusibility of cover. A long melting range is important; it reduces the sensibility to overheating. It is possible to obtain the required property by mixing two different frits in the mill, or by additions of clay, quartz, or feldspar. The coefficient of expansion does not have the supposed importance, the solution of iron being a powerful corrector. For one-layer enamels, the color and aspect must be considered; black ground coats are best. There is a series of desiderata for cover coats, *viz.*, acid resistance, gloss, color, shock resistance, etc. A selection must be made among these properties. A. gives particulars concerning cooking utensils and composition of batches. F.E.V.

System iron–cobalt–copper. WERNER JELLINGHAUS. *Arch. Eisenhüttenwesen*, **10** [3] 115–19 (1936).—The three-compound system iron–cobalt–copper has a complete miscibility in the liquid state. There are 3 groups of alloys: (1) δ-mixed crystals which are separated first in the iron corner and which, in the solid state, change into γ-mixed crystals; (2) alloys containing up to 8% copper which solidify as γ-mixed crystals, with the exception of a small region in the iron corner; and (3) alloys containing 8 to 96% copper which separate primary γ-mixed crystals and solidify as heterogeneous batches of γ-mixed crystals and copper. M.V.C.

Testing of etching baths in enamel manufacture. OTTO WAHLE. *Angew. Chem.*, **49**, 220–22 (1936).—For control of the etching process it is necessary to determine the permissible limit of the amount of iron in the bath, *i.e.*, the point at which a new bath should be prepared. The simplest method for this purpose is measurement by hydrometer. An apparatus for the control of the etching baths is described, and 3 tables are given. E.W.S.

Thermal efficiency of revolving furnaces for melting enamel. OTTO T. KORITNIG. *Emailwaren-Ind.*, **14** [35] 243–45; [36–37] 252–53 (1937).—K. discusses attempts to determine heat transfer through conduction, radiation, and convection in revolving furnaces for enamel melting. M.V.C.

Unusual enamel batches. VIELHABER. *Emailwaren-Ind.*, **14** [48] 331 (1937).—The unusual composition of special enamels formerly used is analyzed. M.V.C.

Zinc oxide. VIELHABER. *Emailwaren-Ind.*, **14** [30] 211–12 (1937).—The viewpoints of various investigators on the effect of zinc oxide on enamels are discussed. Zinc oxide should be regarded as a "quality producer" used to improve the properties of enamel. Zinc oxide used in ceramics must be white and free from impurities. M.V.C.

REPORT

Annual Report of Metallurgical Division. Progress Report No. 20. R. S. DEAN. *U. S. Bur. Mines Repts. Investigations*, No. 3357, 55 pp. Free. R.A.H.

PATENTS

Apparatus for fusing and spraying pulverized substances. FRITZ SCHORI. U. S. 2,108,998, Feb. 22, 1938 (March 12, 1935). A coating apparatus comprises a flame-spraying device for fusible powder having passages therein to conduct and discharge the spray components, including a passage adapted for connection at its entrance end to a supply of air under pressure and having two branches separately leading to the point of flame discharge of the apparatus, fusible powder supply means associated with but one of the branches, and another passage separately leading to the point of flame discharge and adapted for connection to a combustible mixture supply.

Collapsible tube enameling machine. WALTER PRUSSING (Victor Metal Products Corp.). U. S. 2,108,443, Feb. 15, 1938 (April 12, 1934).

Enamel, etc. KURT BEYERSDORFER. Ger. 650,984, Oct. 5, 1937; Cl 48*c*. 2.02; *Chem. Abs.*, **32**, 746 (1938).—Opaque enamels and glazes are made by using the products from fused metals and their oxides as turbidity-producing

substances, the usual setting agents and dispersing agents being added. Thus, a frit of ground SnO_2 is dispersed in fused Sn in the presence of O at 450° until all the Sn is oxidized. The product is made up into a glaze or enamel by mixing with clay and Na perborate. Also, Sb frit is dispersed in fused Sb in the presence of an air current and $NaNO_3$ is added. The product, $NaSbO_3$, is made up as a glaze or enamel as before.

Enamel and glaze. EMIL R. EICHLER. Ger. 650,749, Sept. 30, 1937; Cl. 80*b*. 23.01; *Chem. Abs.*, **32**, 746 (1938).—A substitute gold for use when firing enameled or glazed pottery consists of Cu 1.7 to 2, Zn 2.9 to 4.2, Sb 0.2 to 0.4, Fe 0.5 to 0.7, Pb 1.1 to 3, Bi 0.6 to 1.1, Ni 0.5 to 0.8, Ag 8 to 12, U 1.4 to 2.9, Ti 1.9 to 3.6, Cr 0.46 to 0.91, Mo 0.36 to 0.79, Cd 0.9 to 2.1, and B_2O_3 5.8 to 6.8 parts, applied mixed with a metal resinate solution.

Enamel and glaze. PHILIPP EYER. Ger. 648,092, July 21, 1937; Cl. 48*c*. 2.02; *Chem. Abs.*, **31**, 7212 (1937).—As an opacifying agent for addition to melts of enamels and glazes, use is made of ZrO_2 (or crude Zr ore) in association with powdered glass. A soft glass of high alkali and low CaO content is preferred. Suitable proportions are ZrO_2 about 3 and glass about 5%. The ZrO_2 may be replaced by a product obtained by heating ZrO_2 under oxidizing conditions with another opacifying agent, *e.g.*, Al_2O_3 or Sb_2O_3.

Enameled plaque and method of making. A. F. REILLY (Evans Case Co.). U. S. 2,108,444, Feb. 15, 1938 (Oct. 3, 1935). In an article of the class described, in combination, a metal plate having a design in relief formed thereon, the plate being engine turned, and a coating of enamel on the plate, the surface of the plate having areas of varying depths to produce the design whereby a varying shading effect is imparted by the enamel over the areas.

Enameled sheet-metal heating and cooking vessels. E. STEVENS AND E. STEVENS, LTD. Brit. 479,167 and 479,168, Feb. 16, 1938 (March 11, 1937).

Enameled ware. IGNAZ KREIDL. U. S. 2,109,487, March 1, 1938 (Feb. 12, 1931). Enameled sheet-iron ware comprises a white clouded vitreous enamel and a base consisting of an alloy of iron with not more than 3% of a metal selected from the group consisting of cobalt and nickel but containing a sufficient amount of the metal to cause adhesion of the enamel to the iron base.

Enamels. CHEM. WERKE VORM. H. & E. ALBERT A.-G. (Hans Mengele, inventor). Ger. 648,180, July 24, 1937; Cl. 48*c*. 2.01; *Chem. Abs.*, **31**, 7212 (1937).—Borax used in the manufacture of enamels is replaced wholly or in part by a polyphosphate in which the ratio $Na_2O:P_2O_5$ lies between 2:1 and 1:1.

Method of making lavatories, sinks, wash, or like basins. BRIGGS MANUFACTURING CO. Brit. 479,678, Feb. 23, 1938 (Jan. 27, 1936).

Vitreous enameled products. D. E. KRAUSE (Monsanto Chemical Co.). U. S. 2,109,271, Feb. 22, 1938 (Oct. 5, 1936). A vitreous enameled article comprises a layer of vitreous enamel vitrified upon the surface of a steel sheet, the steel containing from 0.1 to 1.0% of phosphorus, the remainder being iron containing the usual impurities ordinarily occurring in enameling steel.

Glass

Application of glass to piping installations of small diameter and hot-water heaters. K. WIEGAND. *Glastech. Ber.*, **15** [6] 207–19 (1937). J.F.H.

Arsenious oxide as an opacifying agent in lead glasses and the manufacture of China glass in India. ATMA RAM AND LAL C. VERMAN. *Proc. Indian Sci. Congr., 25th Congr.*, **1938**, Part 3, p. 98.—Arsenious oxide, when added to the glass batch to the extent of about 4%, produces dense white opacity in high-lead glasses. For the development of a proper degree of opacity, the molten glass should be allowed to cool very slowly from 700°C. If the resulting glass is cooled suddenly, very little opacity is developed. This opaque glass has been used as a decorative enamel for glass bangles. Cyrolite does not appear to be the proper opacifying agent for preparing such enamels. An addition of 0.1% of antimony oxide to the glass batch appreciably improves the gloss of the enameled design. These glasses are somewhat similar to phosphate opals and appear to be of the "emulsion type." The possibilities of the manufacture of "China glass," an imported milk-white glass used in the Indian glass bangle industry for decorating the bangles, are discussed. A.P.S.

Blank distribution and the penetration factor. GEORGE ROESSLER. *Glass Ind.*, **18** [8] 265–66 (1937).—R. discusses the behavior of melted glass in the blank mold at the time of the blow-back and methods for designing molds to make full use of the ductility and penetration factors. A brief outline of the blown-blown method of forming glass articles is given. Distribution in the blank mold begins with the primary penetration and the time interval of the blow-down; the wall thickness above the filling level depends largely on the speed of the blow-back. The high-water mark can be eliminated by proper use of these two factors. The most common fault in mold design is that of making the blank molds too heavy at the top and too light at the bottom. To obtain proper distribution of mold iron and for constructional reasons, cored slots should be used. E.J.V.

Chemical compounds in glasses. A. APPEN. *Uspekhi Khim.*, **6**, 662–89 (1937); *Chem. Abs.*, **32**, 739 (1938).—Physical properties as a function of chemical composition in both the molten and solid states are discussed for various silicate and borate glasses. A. concludes that glasslike properties are the result of three-dimensional "polymerization," leading to very complex structures, as well as of the type of valence bonds, coördination valence, and the nature of the cation. Glasses can not be regarded simply as mixtures of molecules.

Chemical physics of glass. MARIO CONTI. *Ind. Vetro & Ceram.*, **10** [3] 49–52 (1937).—C. gives fundamentals concerning binary and ternary systems related to glass. Melting phenomena and crystallization are outlined briefly. F.E.V.

Chemistry of glass-furnace construction: I, Slagging processes above the melt. H. JEBSEN-MARWEDEL. *Glastech. Ber.*, **15** [4] 131–36 (1937).—Deterioration frequently takes place where different construction materials come together. Iron parts against refractory can cause

fluxing by oxidation. The mortar especially is susceptible to corrosion by dust from the batch and by alkali vapors. Glaze formed on the refractory runs downward due to gravity, and its composition depends on the reactions taking place as well as the separation of crystalline phases derived from it. The course of the reactions depends on the relative positions of various refractory materials. In the case of sillimanite above silica, this is of particular significance. Some of the products of slagging reach the glass, causing glass faults. Every arrangement of Al_2O_3-containing blocks (especially high Al_2O_3) in the over structure of a glass furnace consisting essentially of silica is apt to cause increased danger of slagging and possible appearance of glass defects. **II, Influence of surface tension of slag glass from refractory material on its tendency to form nodes and cords.** *Ibid.*, [5] 163–73.—The sources of Al_2O_3 containing "drops," nodes, and cords are partly to be looked for in slag streams from above the melt but mainly in the region of contact of glass melt with refractory. Nodes are formed mainly along the horizontal edges at joints and on overhanging surfaces. Drop formation can also take place below the melt surface. From the node formations, "Al_2O_3" threads or cords can form. The appearance and physical properties differ with the type of refractory. The composition of the slag glass is not the result of smooth solution of the refractory. It depends on a process of differentiation resulting from different diffusion velocities and crystallization effects in which some constituents separate as a solid phase. The surface tension as the driving force is important in judging these manufacturing defects. Studies were made using 1-g. samples of glass saturated with sillimanite or clay. A clay solution in glass shows a much greater tendency to form "drops" than a sillimanite solution. The tendency increases with increasing Al_2O_3 and SiO_2 content and with falling temperature. The drawing up of the slag glass into globules due to surface tension removes the protective action of the refractory-saturated glaze on the surrounding surface and permits increased corrosion of the refractory. With a glass series of increasing Al_2O_3 content in intimate contact with a slag glass, the latter would behave as the imbedded glass with the first members of the series. With higher members of the glass series it would tend to be the imbedding or increasing glass phase. The surface-tension relations under such conditions are of considerable importance to processes of homogenization taking place in glass melts. J.F.H.

Determination of the elastic constants of optical glasses from the bending of light by supersonic vibrations. C. Schaefer, L. Bergmann, and H. J. Goehlich. *Glastech. Ber.*, **15**, 447–61 (1937).—Apparatus and theory are discussed in detail. The optical figure obtained consists of two concentric rings which result from light passing through a glass cube subjected to high-frequency vibrations. The inner ring arises from longitudinal and the outer from transverse vibrations. The relation of the radii give directly the cross-sectional contraction coefficients, σ. Calculation of the torsion and elastic moduli, μ and E, respectively, requires knowledge of the density, exciting frequency, and apparatus constants. The latter can be determined in two ways which give results in good agreement. The accuracy of measurement is approximately $\pm 1\%$. A relation between density and elasticity is shown to be present; σ increases with increasing density, while μ and E tend to drop. Special advantages of the new method are (1) lack of secondary effects, as it is a dynamic method; (2) the possibility of obtaining the elastic constants in a closed system directly from a single measurement; and (3) extraordinary rapidity, as little adjustment is necessary in making measurements. J.F.H.

Determining glass strains by spatia' observations in polarized light. M. Ardenne. *Glastech. Ber.*, **15** [8] 299–300 (1937).—The system consists of a light source with a polarizing filter, a special projection screen which does not depolarize, and a pair of spectacles equipped with polarizing filters. J.F.H.

Development of a modern colored glass. Anon. *Glass Ind.*, **18** [8] 263–64 (1937).—Experiments to produce a pure yellow glass uniform in color from pot melt to pot melt, easily worked, and not too expensive are discussed. Since a muddy yellow color was obtained when both cerium dioxide and titanium dioxide were used in a melt, the pure oxides were obtained, and test batches resulted in an excellent color which was constant. A reasonably cheap, almost chemically pure cerium compound was obtained by separation of the cerium hydrate from monazite sand. Neither cerium dioxide nor titanium dioxide separately in pure form imparts any marked color to a soda-lime glass. The yellow color is possibly due to the formation of a cerium titanate [$Ce(Ti_2O_5)_2$] or a cerium titanium silicate [$Ce(TiSiO_5)_2$]. There seems to be a definite relation of one atom of cerium with either 2 or 4 atoms of titanium in the color formations, and the maximum color density is obtained when the ratio is 1:2 of CeO_2 to TiO_2 by weight in a soda-lime glass. E.J.V.

Development of optical glasses. In memory of Otto Schott. W. Weyl. *Angew. Chem.*, **48**, 677–78 (1935).—W. presents a historical treatise on the development of achromatic glasses as well as of glasses for laboratory purposes and for thermometers, emphasizing the share which Otto Schott (1851–1935) had in this development and the difficulties that had to be overcome. Special mention is made of his collaborators, Zeiss and Abbé, as well as of the Zeiss Foundation. See "Schott—," *Ceram. Abs.*, **15** [11] 332 (1936). E.W.S.

Effect of chemical composition of silvering bath on the silvering process. B. N. Moskvin and T. T. Neumann. *Optiko-Mekh. Prom.*, **7** [3] 5–8 (1937); abstracted in *Chem. Zentr.*, **1937, ii**, 4221.—The effect of the concentration of reducing agents (inverted sugar with HNO_3) and of KOH and the effect of temperature on the precipitation of Ag when silvering were studied. The velocity of reduction was found to be most important. The best results were obtained with 0.5% and 1% concentration of the reducers (with a double amount of $AgNO_3$). The temperature should lie between 13° and 18°C. See *Ceram. Abs.*, **17** [2] 61 (1938). M.V.C.

Effect of raw materials on devitrification of quartz glass. M. A. Bezborodov, N. D. Zavyalov, and F. A. Kurlyankin. *Ogneupory*, **4** [10] 638–49 (1936); abstracted in *Referat. Silikatliteratur*, **4** [8] 4360 (1937).—Quartz glass devitrifies at over 1100° and loses its valuable properties. The transformation into the crystalline state, whereby beta-cristobalite changes into alpha-cristobalite with

another specific gravity, destroys the structure of the materials. Therefore, the effect of raw materials used, the temperature, and the duration of heating on devitrification were studied. Various kinds (99% silica) of sand (for nontransparent glass) and rock crystal (for transparent glass) were melted in a vacuum furnace. In all cases, quartz glass begins to devitrify at about 1200°C after 5 hr. heating; cristobalite separates in the temperature range of 1100° to 1500°C after 5 hr. heating; transparent glass devitrifies less than nontransparent quartz glass; and the degree of transformation of nontransparent glass does not depend on whether it is subjected to continuous or intermittent heating but depends only on the duration of heating. M.V.C.

Effect of various factors on the color of copper ruby. V. V. VARGIN AND N. P. KOZHIN. *Keram. & Steklo*, **13** [11] 21–26 (1937).—Fourcault glass can be used for the manufacture of copper ruby with a suitable amount of copper and lead. The glass is of high quality. It may be improved to a certain extent by increasing the silica content and decreasing that of soda or by replacing three parts of CaO by PbO and introducing a small amount of B_2O_3. CaO considerably lowers the quality of the ruby glass by lowering its transparency in the red part of the spectrum. The quality of ruby glass and the intensity of its color (concentration of pigment) do not change equally. Each of them has a maximum which depends on the concentration of copper and lead in the glass. The most suitable content of copper (when introduced into the batch as oxide) and lead is 1.0 Cu and 0.5% Sn or 0.5 to 1.5 Cu and 1.0% Sn. The best glass was obtained with 1.0% Cu and 1.0% Pb. When melting in a large pot, the quantity of lead should be lowered. The quality of ruby glass is considerably diminished by a relatively high concentration of lead and by a large general concentration of copper and lead. The temperature of annealing is of great importance. For a glass of the Fourcault type, the best annealing temperature is about 625°. Higher or lower temperatures impair the quality of glass. The increase of the duration of annealing improves the ruby at first and later has no effect. Defective glass is manufactured apparently by too great a reduction of copper or too high a ratio of Sn to Cu. M.V.C.

Etching effect of lithium nitrate on glass. B. SIEDE. *Glas & Apparat*, **18** [16] 163 (1937).—According to Stewart and Young (*Ceram. Abs.*, **14** [10] 243 (1935)), it is possible to etch glass by molten lithium nitrate. Glasses treated in this manner, however, although a fine white surface was obtained, always broke in spite of the greatest care. Microscopic investigation showed that the etched surface contains numerous fine cracks from which still finer cracks branch out. The glass also undergoes a chemical change, the Na being replaced by Li, whereby the structure is loosened and the expansion coefficient changes and differs from that of the interior glass. This is the cause of the breaking. M.H.

Factors which influence the results of mechanical tests on glass. E. ALBRECHT. *Glastech. Ber.*, **15** [7] 285–87 (1937). J.F.H.

Glass colored by sulfurous matter: V–VI. K. FUWA. *Jour. Soc. Chem. Ind. Japan*, **40** [8] 299–300B; [11] 413–14B (1937).—Sulfide, which under ordinary conditions does not color glass, colors it from yellow to orange in the presence of a reducing agent. For Part IV see "Series—," *Ceram. Abs.*, **16** [11] 335 (1937). M.V.C.

Glass containers for pharmaceutical products. AMBEG. *Eng. Progress*, **18** [12] 271 (1937).—An automatic ampoule-making machine is shown which can make 2000 ampoules and test tubes per hour or 2500 tablet bottles. With slight readjustments the machine can make (1) ampoules with two tips, (2) flat-bottomed ampoules with smooth tips, (3) flat-bottomed ampoules pinched, and (4) round bottomed ampoules. The glass tubing used is inserted in factory lengths and need not be cut. The ampoules are sealed by fusing and sterilized so that they can not become contaminated during transport and storage. J.L.G.

Glasses of special composition. OSCAR KNAPP. *Technikai Kurir*, **8**, 18–20 (1937); *Chem. Abs.*, **31**, 8850 (1937).—The chemical compositions of various glasses are given, with special consideration of the B_2O_3 content. Glasses containing 20% B_2O_3 are transparent to ultra-violet rays. Those containing 30% B_2O_3 and 20% PbO are transparent to X-rays; without B_2O_3, glasses containing 35% PbO retain most X-rays. A glass called Minos, containing 44% PbO, is used for electric condensers because of its high dielectric constant. Euphos glass, containing TiO_2, V_2O_5, or Cr_2O_3, absorbs all ultra-violet rays.

Glass fibers for glasshouse needs. ANON. *Glass Ind.*, **18** [11] 373–76 (1937).—Glass fibers of two general types are now produced: long textile fibers 0.00025 in. in diameter and shorter insulating wool fibers about 0.0004 in. in diameter. This glass fibrous insulation has a conductivity of 0.27 B.t.u./sq. ft./hr./in. thickness/°F difference in temperature between the hot and cold sides. An economical building structure has been developed by using a steel framework and placing 4 in. of fiber insulation between two sheets of corrugated iron. The fibers start to soften at about 1000°F; their use for insulation at over 900°F, therefore, is not recommended, although excellent results are obtained in insulating portions of leers, ovens, and kilns where the temperature is under 900°F. Various applications of glass-wool insulation are described. E.J.V.

Glass as industrial replacement material: Suggestions of the Technical Committee of the hollow glass industry. F. WECKERLE. *Glastech. Ber.*, **15** [6] 196–201 (1937). J.F.H.

Glass for new applications. H. MAURACH. *Glastech. Ber.*, **15** [6] 195 (1937). J.F.H.

Glass in the physics of building construction. H. REISNER. *Glastech. Ber.*, **15** [12] 463–65 (1937). J.F.H.

Glass sands. S. R. SCHOLES. *Glass Ind.*, **18** [9] 293–97 (1937).—Modern glass sand is practically a chemically pure reagent, containing, in general, only one undesirable impurity, iron. Specifications for glass sand can be drawn up partly with a view to what the glassmaker actually needs and partly with a sample description of what can be had. No. 1 glass sand is expected to contain not less than 99.5% SiO_2, not more than 0.3% Al_2O_3, less than 0.1% CaO and MgO, and less than 0.025% Fe_2O_3. All of the sand will pass 20-mesh, varying in fineness beyond that. The permissible iron content must depend upon the character or "color" of the glass to be produced. Occurrence

and methods of working of the different types of glass sand deposits are discussed in detail. The Oriskany quartzites outcrop throughout the Appalachians and are very hard, while the softer St. Peter sandstone is found in a state of high purity in Ill. and Mo. In some plants a sand produced from a somewhat inferior rock is treated with hot concentrated sulfuric acid for the removal of Fe_2O_3, which greatly improves the quality of the sand. Illustrated. E.J.V.

Glass as a substitute: Experiences of a glass factory. G. SCHOTT. *Glastech. Ber.*, **15** [6] 202–207 (1937). J.F.H.

Glass as substitute for other materials of construction from the standpoint of the user. M. MENGERINGHAUSEN. *Glastech. Ber.*, **15** [6] 201–202 (1937). J.F.H.

Glass wool—from raw material to fabric. P. KRÜGER. *Deut. Textilwirt.*, **4** [15] 6–10 (1937); *Chem. Abs.*, **31**, 7613 (1937).—K. gives a description of properties, preparation, manufacture, and uses. Glass threads, yarn, and fabrics are shown. 22 illustrations.

Gold-ruby glasses: I. W. GANZENMÜLLER. *Glastech. Ber.*, **15** [9] 346–53 (1937).—It was known to alchemists of the Middle Ages that red colors could be produced by gold, but as yet no proof of the preparation of gold-ruby glasses in this period has been discovered. 55 references. **II.** *Ibid.*, [10] 379–84.—The first definite mention of gold-ruby glasses is found in Italian writings of the early part of the 15th Century. J.F.H.

Homogenizing glass in tank furnaces. E. BAYER. *Glashütte*, **67** [45] 691–92 (1937).—B. describes a new tank furnace which promotes homogenization of the glass batch. The bottom of the glass tank is provided with cross bars which increase the flow over the bottom and therefore promote melting. M.V.C.

Industrial and structural products laboratory of the Owens-Illinois Glass Co. H. C. WINSOR. *Ind. Eng. Chem., Anal. Ed.*, **10** [1] 42–44 (1938).—Prominent features in the construction of the laboratory are described and illustrated. F.G.H.

Magnesia as a raw material for glass. ZSCHACKE. *Glashütte*, **67** [42] 643–45 (1937).—Advantages of a partial replacement of CaO by MgO by additions of dolomite are as follows: (1) it is easier to melt and work the glass; (2) the addition of dolomite lowers the alkali content and therefore increases stability, and purification of the glass will be much easier; (3) magnesia has no effect on the glass color; (4) MgO has a low coefficient of expansion, and glass containing dolomite is more resistant to mechanical and thermal effects than a corresponding lime glass; (5) the danger of devitrification is minimized. Twenty-nine batches for various types of glass are analyzed. M.V.C.

Manufacture of rosaline glass in tank furnaces. G. YU. ZHUKOVSKIĬ AND V. V. POLLYAK. *Keram. & Steklo*, **13** [12] 6–13 (1937).—Acid glass compositions containing small quantities of alkaline earth oxides (up to 6%) are preferred for obtaining pure rosaline glasses. It is advisable to replace part of Na_2O (from 2.0 to 2.5%) by K_2O, although not absolutely necessary. A lower concentration of selenium is preferable to a high one, providing greater purity of color; 20 g. of selenium are entirely sufficient for 100 kg. of glass mass. An addition of saltpeter is necessary. The addition of arsenic has no marked results on the purity of color in the limits of the concentration of iron oxide used in the experiments. It is possible that, in glasses having less Fe_2O_3, arsenic is a sufficiently powerful agent to neutralize the effect of iron. The addition of Sb_2O_3 is very useful for stabilization of the color in subsequent thermal operations. The glass should contain the least possible amount of iron, and any measure to lower its concentration (raw materials, refractories, etc.) is of the utmost importance. The production of pure rosaline glass containing selenium requires a high temperature, at least 1420°, and a weakly oxidizing atmosphere. The effect of the type of tank furnace has not been studied; tanks of low depth, however, are preferable. Rosaline glass is more suitable for pressed ware than for blown ware. Repeated heating of the glass affects its color. The annealing temperature of rosaline glass should be from 475° to 480°C. A uniform distribution of temperature in the annealing furnace and a strict conformance to the curve of annealing are necessary. The following should be studied further: (*a*) effect of furnace type and flows on the coloring of rosaline glass; (*b*) quantitative study of the ratios of various degrees of oxidation of Se in dependence on melting, working, and annealing; (*c*) conditions for obtaining rosaline colors in glass with a variable iron content; and (*d*) effect of chlorides, particularly common salt, on the stabilization of rosaline color. M.V.C.

Maximum grain size of sand for glassmelting. S. YA. RAF. *Keram. & Steklo*, **13** [12] 13–17 (1937).—The highest rate of melting and purifying of ordinary glass is obtained when using medium-sized sand (0.385 to 0.120 mm.). A batch containing small-sized sand is melted more rapidly; the purifying of the glass from bubbles, however, takes a longer time so that the total duration of melting is increased by 1 hr. The lowering of the amount of dust-like sand particles (0.12 mm.) does not have any effect on melting time. Coarse-grained sand greatly increases the time of melting and purifying. When melting glass in pots, not more than 10 to 12% of the sand should be coarse-grained (0.5 mm.). M.V.C.

Mechanical strength properties of glasses. A. SMEKAL. *Glastech. Ber.*, **15** [7] 259–70 (1937).—S. shows that the breaking process begins with a primary rupture which starts from a flaw and is strongly affected by molecular thermal changes. Secondary rupture surfaces follow, as breaking progresses, as a result of natural inhomogeneities always present. Numerous submicroscopic fissures of the order of magnitude of 10^{-5} to 10^{-6} cm. are irregularly distributed in glass. It is proposed that these result from a shrinkage taking place in the glass below the softening point which is conditioned by viscosity and involves molecular changes occurring in the softening range. 28 references. J.F.H.

Michael Joseph Owens. ANON. *Bull. Amer. Ceram. Soc.*, **17** [3] 148–51 (1938).

Nephelite "worms"—their cause and cure. ANON. *Glass Ind.*, **18** [12] 417–18 (1937).—Nephelite in the "worm" form appears as a brown wormlike stone surrounded by a cordy area of glass and is usually associated with a streamer-type cord. Nephelite is the low-temperature phase of the mineral having the theoretical composition $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$. Nephelite may be formed by the

combination of soda with materials containing alumina and silica, *e.g.*, clays and refractories, by the reaction of a soda silicate glass with alumina, or from intermediate compositions which contain the necessary soda, alumina, and silica. The formation of nephelite in the "worm" form is generally caused either by the incomplete solution in the glass of silica drippings which have been in contact with soda and alumina or by recrystallization from cords which were originally nephelite or which have the composition necessary for its formation. The methods of formation of nephelite are discussed at length. Formation of the nephelite "worm" type of stone may be prevented or at least minimized by the substitution of aluminous material for silica, where the latter is subjected to excessive temperatures and batch dust, and by the elimination of excessive fluxing of the silica brick resulting from improper control of the furnace. This requires frequent and continued check-up of the condition of the inside of the furnace, and a close watch must be kept on the various factors such as flame direction, etc., that cause the rapid formation of corrosive, alkaline, silicate liquids. E.J.V.

Phosphate coloring by metallic atoms and coloring of phosphate glass permeable to ultra-violet rays by phosphorus atoms. JOSEF HOFFMANN. *Sprechsaal*, **70** [41] 517–19; [42] 529–31 (1937).—Heretofore unknown discolorations due to exposure of various phosphorus compounds are described. The red coloration on exposure of phosphate glasses permeable to ultra-violet rays is accounted for by phosphorus atoms. This atomic coloration is a counterpart of the coloration by silicon, arsenic, and antimonate atoms. The assumption that it is actually due to phosphorus atoms and not to alkaline or alkaline-earth atoms is confirmed by the results of experiments on (1) coloring by means of metallic vapors, (2) decoloration of red phosphorus at the ignition temperature, (3) effect of ultra-violet rays, (4) similarity with phosphorus sols known, and (5) destruction of color by oxidizing heating and by fumes of nitric acid. M.V.C.

Plasticity and viscosity of glasses. Points of transformation. P. BARY AND J. HERBERT. *Ind. Chim. Belge*, **8** [12] 502–10 (1937).—When progressively heated, all vitreous substances show a definite point of transformation (T_1) which is characterized by a sudden variation of the physical properties of the experimental sample. In regard to glasses, this point of transformation marks the separation between the solid state and the plastic state of the material. At a temperature 400° to 500°C above that corresponding to T_1, there seems to exist another point of transformation (T_2), when the glass fluidity is sufficient to allow the metal to flow. Knowledge of the existence of T_1 and T_2 is of great technological interest since the corresponding temperature interval represents the working range of the metal. An attempt is made to apply factors for calculating T_1 and T_2. Assigning to viscosity, for glass in the solid state, the value 10^{13} (the viscosity curve is that of an exponential function, but the value of η changes from 10^{13} to ∞ for such a slight drop of temperature that it can hardly be figured with accuracy) and plotting $\log \frac{10^{13}}{\eta}$ (in ordinates) against $\log T$ (in abscissas), one obtains a series of points of the representative curve of the function. In the case of soda-lime glasses, these curves are practically parallel straight lines; by lengthening them downward, these lines strike the axis of abscissas on which they determine the positions of points T_1. The equation of the function is $\log \frac{10^{13}}{\eta} = A \log \frac{T}{T_1}$, where T is the temperature of experimentation, while $A = 36.1$ in the case of CaO–Na_2O–SiO_2 glasses. The experimental determination of T_2 is seriously affected by the rate of heating the metal, and the values obtained also depend on the thermal history of the glass sample. T_2 is given by the formula $\log T = \frac{8.2}{36.1} + \log T_1 = 0.227 + \log T_1$, or graphically by lengthening the viscosity curve upward until it strikes a parallel line to the axis of abscissas, cutting the axis of ordinates at a point corresponding to $\log \frac{10^{13}}{\eta} = 8.2$. Comparative data obtained either by experimentation or by computation are tabulated; in some cases, results agree very satisfactorily. The method has also been applied to MgO-, Al_2O_3-, and PbO-soda glasses, sometimes with satisfaction. Glasses are considered as colloid systems; the variation of their physical properties, as a function of temperature, is strongly influenced by the time factor; in the solid state, glass consists of an irregular and intricate lattice of calcium silicate polymerized molecules, the interstices of which are filled with more fusible sodium silicate; under the action of heat, polymerized molecules gradually break up. See *Ceram. Abs.*, **16** [11] 335 (1937). R.W.D.

Preparation and use of glass textile fabrics. L. VON REIS. *Glastech. Ber.*, **15** [6] 219–28 (1937). J.F.H.

Preparing articles of vitreous silica by new methods. F. SKAUPY AND G. WEISSENBERG. *Glastech. Ber.*, **15** [8] 306–308 (1937).—The preparation of articles of vitreous silica is usually accomplished at present by the Bottomley method, the resulting large hollow mass being later worked into smaller articles. By the new method, which is largely well-known ceramic technique, powdered quartz is pressed to form with or without a binder. Firing is carried out at such a temperature that the initially crystalline particles become glassy and fuse together. Some precautions are necessary to care for changes in crystal form and to avoid devitrification. J.F.H.

Properties of glass fibers. W. EITEL AND F. OBERLIES. *Glastech. Ber.*, **15** [6] 228–31 (1937). J.F.H.

Properties of silicate glasses in comparison with transparent synthetic materials. W. EITEL. *Glastech. Ber.*, **15** [4] 137–41 (1937).—The organic and inorganic glasses for particular applications have certain advantages and disadvantages. A general replacement of the inorganic glasses by transparent resins will never occur. The silicate glasses have the great advantage of more thorough adaptability of their properties, such as optical constants, through composition. Their greater homogeneity is important in electrical applications. The transparent plastics may have advantages in many applications because of lower specific gravity, but lower surface hardness is a disadvantage. J.F.H.

Sensitive glass electrode of durable form. ANGUS E. CAMERON. *Ind. Eng. Chem., Anal. Ed.*, **9** [9] 436 (1937).—

Details for the construction of an electrode of low resistance and rugged form are given. Illustrated. F.G.H.

Specific gravity of CaO–Na_2O–SiO_2 glasses at high temperature: I. I. SAWAI AND S. INOUE. *Jour. Soc. Chem. Ind. Japan*, **40** [6] 198–200B (1937).—Glass of the following composition was studied: 65.53 SiO_2, 19.71 CaO, 0.61 Al_2O_3 + Fe_2O_3, 14.15% Na_2O. Specific gravity changes with temperature. The curve has a break lying near the softening point of the glass. M.V.C.

Story of vitreous china. GEORGE BRAIN. *Jour. Inst. Sanitary Engrs.*, **41**, 155–67 (1937); *Chem. Abs.*, **31**, 8855 (1937).

Technical snapshots of glass. H. JEBSEN-MARWEDEL. *Z. Wiss. Mikroskop.*, **54**, 197–204 (1937); *Chem. Abs.*, **31**, 8849 (1937).—Crystals, bubbles, striae, and various surface defects and markings are illustrated and discussed briefly.

Tempering and reheating of boric anhydride glass. E. RENCKER. *Compt. Rend.*, **205** [26] 1396–98 (1937).—The volume of a boric anhydride glass above 260°C depends on its previous thermal history, but after a period of evolution, sometimes very long, the volume tends toward a definite value at each temperature. A curve shows this volume for temperatures up to 300°. It has been observed that anomalies of physical properties of all vitreous substances occur at the same temperature at which they soften. R. calls them properties of "vitreous fusion." See "Dilatometric—," *Ceram. Abs.*, **17** [4] 137 (1938). M.H.

Textile processes in the production of glass fibers. P. KRÜGER. *Glastech. Ber.*, **15** [12] 461–63 (1937). J.F.H.

Trouble shooting and the penetration factor. GEORGE ROESSLER. *Glass Ind.*, **18** [9] 298–300 (1937).—In the fabrication of glassware, the ductility of molten glass and the penetration factor supply a simplified technology by which the erratic and seemingly mysterious behavior of the glass in the mold can be governed with a reasonable degree of accuracy. The practice, in designing blank molds, is to calculate the cavity of a size or volume which is in a certain ratio to the volume of the solid mass of glass, to lay out the length of the parison so as to allow for the stretch and sag during the interval of transfer, and to make the various cross-sectional contours in proportion, roughly, to the corresponding cross-sections of the finish mold. The glass is in contact with the iron while the finish is being made and penetration takes place; the hot inner area of the glass is then blown back. The parison, therefore, is comparatively cold at the shoulder but very hot at the bottom end since it is made of the hot inner glass. In the lower range of working temperatures of glass, slight changes of temperature make decided changes in ductility, and therefore the parison must be designed in size and proportions so as to compensate for these variations in ductility. Control of the ductility characteristic of melted glass, through a control of the penetration factor, is the means by which the glass of the parison can be controlled in its relative disposition. A few of the more common difficulties are discussed together with the principles involved. E.J.V.

Two-phase glasses: I, Method of determining the thermal properties of glass. IKUTARO SAWAI AND IKUZO KUBO. *Mem. Coll. Eng. Kyoto Imp. Univ.*, **10**, 1–5 (1937).—The method of constructing and calibrating a special electrically heated furnace for determining the thermal properties of glass is described. **II, Copper ruby glass.** *Ibid.*, pp. 6–9; *Chem. Abs.*, **31**, 8849 (1937).

Vitreous state of glass. JÁNOS SÖRÖ. *Technikai Kurir*, **8**, 69–71 (1937); *Chem. Abs.*, **31**, 8850 (1937).—On the basis of examination of the crystal lattices of various kinds of glass and the heat of formation of glass, the following oxides can be considered as glassforming: B_2O_3, P_2O_3, As_2O_3, Sb_2O_3, Al_2O_3, SiO_2, GeO_2, Sb_2O_5, As_2O_5, P_2O_5, V_2O_5 Cb_2O_5, and Ta_2O_5. Besides these, other oxides can be added to glasses to produce a characteristic effect on the properties. This effect is probably due to disturbance of the tetrahedric structure of ordinary glass. All precious stones except diamond consist of the above-named glassforming oxides.

Volatilization of boric anhydride in glass. V. V. VARGIN. *Optiko-Mekh. Prom.*, **6** [9] 14–16 (1936); abstracted in *Chem. Zentr.*, **1937, ii**, 4222.—The volatilization of B_2O_3 during the melting of glass batches containing B_2O_3 is accounted for by the volatilization of boric acid with steam; at 500°C, 5.6% boric acid is evaporated from $B(OH)_3$; under the same conditions, no volatilization was detected from waterless B_2O_3. In a moist batch of the composition 32.5 SiO_2, 13 B_2O_3, 3 Al_2O_3, and 51.5% BaO, 3.11% boric acid evaporated at the beginning of melting, while only 0.1% of the B_2O_3 present volatilized during 8 hr. of melting at 1400°. M.V.C.

X-ray investigations of the fine structure of glasses: I, Review of experimental results obtained by X-ray researches on glass. E. SCHIEBOLD. *Glastech. Ber.*, **15** [6] 231–40 (1937).—Previous work is critically reviewed. Attention is called to the work of N. Valenkov (*Ceram. Abs.*, **16** [8] 242 (1937)). Using nickel filtered radiation with a short-radius camera, he obtains results favoring the crystallite theory n contrast to the conclusions of Warren (see "X-ray—," *ibid.*, **17** [2] 87 (1938); "Structure—," *ibid.*, [3]101). 33 references. J.F.H.

BOOK

Modern Fine Glass. LELOISE DAVIS SKELLEY. Richard R. Smith, New York. 144 pp. 97 photographs. Price $5.00. Reviewed in *N. Y. Times Book Review*, Feb. 6, 1938.—Glass of the modern era has exquisite beauty. S. not only presents the decorative glass of Europe and America at the present time but leads up to these modern achievements in a brief and remarkably comprehensive chapter of historical summary. "Virtually every attribute of lovely glass is a residual product of centuries of toil and experimentation, slowly evolving through the heat of the furnace and the minds of men." S. traces the development of the famous old glass of Venice and of Bohemia on to today, and the distinctive work which is the product of the government industrial schools of Czechoslovakia is emphasized. In the chapter on French glass, the contributions of individual artists are stressed. The remarkable and recent history of fine glass production and the activities of various factories in Sweden are recorded. Glassware of Germany, Finland, Holland, Belgium, and Mexico is also described. The chapters on the glass of America are especially interesting. This is a book for every one who is interested in gaining knowledge, general and yet sufficient in particular, of an outstanding art of today.

M.V.C

PATENTS

Apparatus for:

Bending glass sheets. H. J. Galey (Pittsburgh Plate Glass Co.). U. S. 2,111,392, March 15, 1938 (April 27, 1937). William Owen (Pittsburgh Plate Glass Co.). U. S. 2,111,370, March 15, 1938 (Dec. 19, 1936).

Coating electric-lamp bulbs on both sides with paraffin wax, prior to opacifying. Rudolf Maczejka. Austrian 149,980, June 25, 1937; Cl. 32*c*; *Chem. Abs.*, **31**, 7210 (1937).

Drawing glass strips. Andrew Jollie (Pilkington Bros., Ltd.). Can. 371,332, Jan. 18, 1938 (Oct. 13, 1936). G.M.H.

Drawing sheet glass. J. B. Watt (Pilkington Bros., Ltd.). Can. 371,333, Jan. 18, 1938 (Dec. 11, 1936). G.M.H.

Feeding molten glass to glassforming machines. T. C. Moorshead (United Glass Bottle Manufacturers, Ltd.). U. S. 2,111,293, March 15, 1938 (Oct. 25, 1935).

Making nonsplintering glass. Adolf Kämpfer. Ger. 648,305, July 28, 1937; Cl. 39*a*. 17.50; *Chem. Abs.*, **31**, 7210 (1937).—Means for removing solvent from the intermediate layer is described.

Making sheets of glass. Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey. Fr. 811,481, April 15, 1937; *Chem. Abs.*, **32**, 742 (1938).

Making sheets of glass by drawing. N. V. Hollandsche Mij. voor de Vervaardiging van Glas (M. H. L. Halbach, applicant in U. S.). Fr. 815,295, July 8, 1937; *Chem. Abs.*, **32**, 1064 (1938).

Producing bands or fibers of glass, etc. Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey. Fr. 814,149, June 17, 1937; *Chem. Abs.*, **32**, 742 (1938).

Removing lengths from a moving strip of glass. Joseph Gaskell (Pittsburgh Plate Glass Co.). U. S. 2,111,393, March 15, 1938 (May 27, 1936).

Surface treating glass containers. A. G. Lauck and J. M. Johnson (Owens-Illinois Glass Co.). U. S. 2,109,391, Feb. 22, 1938 (July 29, 1936).

Tempering glass. Corning Glass Works. Fr. 812,866, May 19, 1937; *Chem. Abs.*, **32**, 1064 (1938).

Automatic feeding device for glassmelting furnaces. Keramische Industrie-Bedarfs-A.-G. Ger. 648,204, July 24, 1937; Cl. 32*a*. 5; *Chem. Abs.*, **31**, 7210 (1937).

Automatic machine for manufacturing ampullas from glass tubes. Jakob Dichter. U. S. 2,110,327, March 8, 1938 (June 29, 1934).

Building block. W. P. Zimmerman and M. K. Holmes (Owens-Illinois Glass Co.). U. S. 2,110,900, March 15, 1938 (May 26, 1936).

Circular annealing furnace for parabolic glass mirrors. E. Ya. Yurchenko. Russ. 43,137, May 31, 1935; *Chem. Abs.*, **31**, 7615 (1937).—Construction details are given.

Dental plates. Corning Glass Works. Fr. 814,427, June 23, 1937; *Chem. Abs.*, **32**, 1065 (1938).—These are made of opaque colored glass with porcelain teeth embedded therein. A suitable glass contains SiO_2 58.3, Na_2O 7.2, B_2O_3 8.5, Al_2O_3 7.3, CaO 7.7, ZnO 2, Au 0.0375, and F 6.7%. The molded glass is treated with a mixture of HF and H_2SO_4, the teeth being protected by wax.

Device for making bifocal glasses. F. W. O. Wernicke and B. R. Muller (trading as Wernicke Maschinenfabrik). Brit. 480,331, March 2, 1938 (Oct. 30, 1935).

Dual orifice feeder. F. L. O. Wadsworth (Ball Bros. Co.). U. S. 2,108,517, Feb. 15, 1938 (Oct. 24, 1934; June 24, 1935).

Fiber production from molten glass. Piero Modigliani (N.V. Mij. tot Beheer en Exploitatie van Octrooien). Can. 371,659, Feb. 1, 1938 (March 2, 1937). G.M.H.

Frosting of glass articles. Karl Duldner and Roman Wadelka (General Electric Co.). U. S. 2,110,117, March 1, 1938 (June 26, 1937). The process of partially frosting the surface of glass objects, more particularly electric-light bulbs, covering and flashing glasses, lamp shades, etc., comprises applying glass powder to the surface to be frosted to form thereon a pulverous layer, the particles of which are capable of softening at a temperature lower than the softening point of the glass object but incapable of becoming, at a temperature materially below the softening point of the object, so liquid as to coalesce; removing the powder from the parts of the surface that are to remain clear in the finished product; subjecting the surface, together with the remaining powder applied thereto, to a heat treatment at a temperature at which the particles of the powder frit to the surface and form a great number of minute prominences thereon; and thereafter treating the surface with a glass-dissolving agent so as to remove, at least for the greater part, the fritted-on particles from the surface, the duration and intensity of the last-mentioned treatment being so chosen that after this treatment is terminated there remains a partially frosted glass surface provided with minute light-diffusing depressions on its frosted parts.

Furnace for melting glass. Glashütte Achern A.-G. Ger. 651,687, Oct. 18, 1937; Cl. 32*a*. 4; *Chem. Abs.*, **32**, 742 (1938).

Glass. Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey. Fr. 812,308, May 7, 1937; *Chem. Abs.*, **32**, 1063 (1938).—The glass is cooled rapidly before it leaves the furnace by means of a cooled screen placed in the furnace above the glass and protecting the opening.

Glass article manufacture. T. F. Pearson (Crown Cork & Seal Co., Inc.). Can. 371,465, Jan. 25, 1938 (Sept. 15, 1936). G.M.H.

Glass bottle forming apparatus. T. F. Pearson (Crown Cork & Seal Co., Inc.). Can. 371,466, Jan. 25, 1938 (Sept. 15, 1936). G.M.H.

Glass bottle or jar manufacture. T. F. Pearson (Crown Cork & Seal Co., Inc.). Can. 371,621, Feb. 1, 1938 (Sept. 15, 1936). G.M.H.

Glass brick wall. W. O. Lytle (Pittsburgh Plate Glass Co.). U. S. 2,110,885, March 15, 1938 (Oct. 31, 1936).

Glass container. Charles Welhart (Owens-Illinois Glass Co.). U. S. 2,111,499, March 15, 1938 (July 22, 1936).

Glass fibers. N. V. Mij. tot Beheer en Exploitatie van Octrooien. Fr. 813,485, June 2, 1937; *Chem. Abs.*, **32**, 1063 (1938).—The fibers coming from the molten mass are carried along by an aspirating current of gas and deposited on a support which is permeable to the gas.

Glassmelting furnace. W. A. MORTON (Amco, Inc.). U. S. 2,110,736, March 8, 1938 (April 19, 1934).

Glass-to-metal annealing process. HOWARD SCOTT (Canadian Westinghouse Co., Ltd.). Can. 371,300, Jan. 18, 1938 (Aug. 7, 1936). G.M.H.

Glass roofing. AKT.-GES. FÜR GLASINDUSTRIE VORM. F. SIEMENS AND J. SCHLOSINGER. Brit. 479,589, Feb. 23, 1938 (July 26, 1937).

Glass sheet, method and apparatus for making. H. A. FISHER. U. S. 2,108,811, Feb. 22, 1938 (Aug. 24, 1935). (15) The methdd of manufacturing variegated glass sheets comprises providing a body of molten glass of base appearance and a source of molten decorative glass; forming and flowing a molten stream of the decorative glass of relatively small transverse dimension with respect to the width of the body of base glass onto the latter at a point spaced inwardly from the edge of the body of base glass; embedding the decorative glass in the base glass, while the glass is in workable condition, with a surface of the decorative glass exposed at the surface of the base glass; providing relative movement between the base glass and the stream; and finishing the glass into a smooth-surfaced sheet with a decorative area in the base glass of materially less width than the width of the sheet and with the exposed surface of the decorative area in the plane of the surface of the base glass.

Glass tank. P. F. KUZ'MICH. Russ. 42,672, April 30, 1935; *Chem. Abs.*, **31**, 7615 (1937).—Construction details are given.

Glass tempering apparatus. J. L. DRAKE (Libbey-Owens-Ford Glass Co.). Can. 371,150, Jan. 11, 1938 (Dec. 30, 1936). G.M.H.

Glassware forming machine. FRANK O'NEILL (Hartford-Empire Co.). U. S. 2,111,296, March 15, 1938 (Aug. 30, 1935).

Glazed roofing. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Brit. 479,877, Feb. 23, 1938 (Aug. 24, 1935).

Hardened vitreous article. W. J. TENNANT (American Optical Co.). Brit. 478,759, Feb. 9, 1938 (Nov. 3, 1936).

Joining quartz articles to surfaces of metal, glass, or ceramic material. PATENT-TREUHAND-GES. FÜR ELEKTRISCHE GLÜHLAMPEN M. B. H. (Hans Pulfrich, inventor). Ger. 650,446, Sept. 23, 1937; Cl. 32*b*. 10; *Chem. Abs.*, **32**, 1066 (1938).—A layer of a refractory metal, *e.g.*, W, is first secured to the quartz by sintering, and the surface to which the quartz is to be joined is then united, *e.g.*, by brazing, with the sintered layer. Various methods of procedure are indicated.

Laminated article. J. W. HAUGHT (E. I. du Pont de Nemours & Co.). U. S. 2,109,587, March 1, 1938 (Dec. 7, 1935). Laminated glass comprising a sheet of glass and, bonded thereto, a plastic sheet comprising 100 parts of cellulose nitrate and about 85 parts of dibutyl hexahydrophthalate.

Low expansion glass composition. H. P. HOOD (Corning Glass Works). U. S. 2,109,641, March 1, 1938 (Feb. 19, 1935). A glass containing silica, boric oxide, lithia, and at least one other alkali-metal oxide, the silica content being between 75 and 87%, the total alkali content being between 0.5 and 2.5%, and the lithia constituting not over $^1/_3$ of the total alkali content.

Machine for the manufacture of glass articles. T. F. PEARSON. Brit. 478,737, Feb. 9, 1938 (June 23, 1936).

Machines for molding glass. THOMAS F. PEARSON. Fr. 813,789, June 8, 1937. Fr. 813,804 and 813,805, June 9, 1937. Fr. 813,950, June 11, 1937; *Chem. Abs.*, **32**, 1064 (1938). UNITED GLASS BOTTLE MANUFACTURERS. Fr. 813,731, June 8, 1937; *Chem. Abs.*, **32**, 1064 (1938).

Manufacture of laminated glass. W. W. TRIGGS (Hercules Safety Glass Co., Ltd.). Brit. 480,255, March 2, 1938 (Aug. 18, 1936).

Means for forming glass molds. W. V. FISHER (Anchor Hocking Glass Corp.). U. S. 2,110,360, March 8, 1938 (Aug. 17, 1935).

Means for supporting large glass plates during thermal treatment. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Ger. 650,497, Sept. 23, 1937; Cl. 32*a*. 30; *Chem. Abs.*, **32**, 1064 (1938).

Method and apparatus for severing molten glass. F. L. O. WADSWORTH (Ball Bros. Co.). U. S. 2,108,518, Feb. 15, 1938 (Aug. 28, 1933; June 16, 1934; renewed Jan. 7, 1937).

Method of stabilizing annealed glass articles, particularly thermometers. CORNING GLASS WORKS. Brit. 479,631, Feb. 23, 1938 (Dec. 30, 1935).

Multicellular glass. SOC. ANON. DES MANUFACTURES DES GLACES & PRODUITS CHIMIQUES DE ST. GOBAIN, CHAUNY & CIREY. Fr. 46,886, Oct. 30, 1936; *Chem. Abs.*, **31**, 8144 (1937). Addition to 786,818 (*Ceram. Abs.*, **15** [8] 239 (1936)).—A mixture of powdered glass and charcoal is heated to the softening temperature of the glass and maintained at that temperature until the required swelling takes place. The density of the product is regulated by the amount of charcoal added.

Optical glass. SENDLINGER OPTISCHE GLASWERKE G.M.B.H. (George Jaeckel, inventor). Ger. 650,280, Sept. 17, 1937; Cl. 32*a*. 28; *Chem. Abs.*, **32**, 1064 (1938).—A description is given of a method of cooling a tank containing fused glass, as a step in the manufacture of optical glass.

Optical glass. SENDLINGER OPTISCHE GLASWERKE G.-M.B.H. Fr. 812,925, May 20, 1937; *Chem. Abs.*, **32**, 1064 (1938).—After removal from the furnace, the fusion pot filled with homogenized glass is first cooled so that the base and walls of the pot are subjected to a rapid cooling while the top surface of the glass is maintained continuously at the temperature of the center of the glass by means of a heating plate applied thereto. The temperature of the heating plate is progressively reduced to the temperature of the insulating envelope when the slow cooling begins.

Photoluminescent glass. I. G. FARBENIND. A.-G. Fr. 47,478, May 22, 1937; *Chem. Abs.*, **31**, 8144 (1937). Addition to 792,844 (*Ceram. Abs.*, **16** [11] 338 (1937)).—The constituents containing Sn as the excitable metal, with or without other excitable metals, are fused under oxidizing or neutral conditions.

Process for the manufacture of tempered glass. C. T. PUGH AND W. ASH. Brit. 478,811, Feb. 9, 1938 (Nov. 15, 1937).

Ruby glass. DEUTSCHE GOLD- UND SILBER-SCHEIDEANSTALT VORM. ROESSLER (Hans Löffler, inventor). Ger. 651,928, Oct. 22, 1937; Cl. 32*b*. 2; *Chem. Abs.*, **32**, 742

(1938).—Ruby glass or enamel is prepared by adding Se and Cd exclusively as CdSe. Sulfidic S and Zn are also added. Thus, ruby glass is made by heating sand, CdSe, ZnS, and ZnO to 1350°. Another example is given.

Tempered glass articles. Corning Glass Works. Brit. 479,173, Feb. 16, 1938 (Sept. 24, 1935).

Tempering glass. Soc. Anon. des Manufactures des Glaces & Produits Chimiques de St. Gobain, Chauny & Cirey. Brit. 479,878, Feb. 23, 1938 (Sept. 5, 1935).

Structural Clay Products

Brick has lowest maintenance expense. Annual Report of Director of Public Works, Richmond, Va., 1936. Anon. *Dependable Highways*, No. 156, p. 9 (1937).—Maintenance data have been assembled in tabular form. The insignificant maintenance expense of brick pavements is compared with the expense of other types. See *Ceram. Abs.*, **17** [4] 141 (1938). P.S.D.

Brickmaking plant. Anon. *Mech. Handling*, **24**, 117–19 (1937).—The plant at the Childerditch works of the Essex Brick Co., Ltd., which produces 6000 brick per hr. by the "semidry" process, is described. J.C.C.

Brick pavement for new Lincoln Tunnel. Anon. *Dependable Highways*, No. 155, p. 2 (1937).—The use of de-aired vertical-fiber paving brick throughout the entire length of the new Lincoln Tunnel is briefly described. P.S.D.

Brick and tile coloring. Felix Singer. *Brit. Clayworker*, **46** [550] 389–92 (1938).—S. discusses engobes, their uses, and methods of applying them. R.A.H.

Economical handling in brickworks. Anon. *Mech. Handling*, **24**, 219–20 (1937).—An overhead conveyer may be used to advantage for handling loaded wheelbarrows from the drier to the kilns and returning them when empty. J.C.C.

Effect of the freezing test on the strength of brick. O. Drögsler. *Tonind.-Ztg.*, **61** [52] 577–78 (1937).—Since the standard test of 25 freezing cycles does not always show enough difference in the appearance of brick, the testing of the brick for strength after the freezing tests is recommended. D. discusses tests of transverse, compressive, and shearing strength on six kinds of brick before and after 25 and 50 freezing cycles and the difference in the modulus of rupture between full-size brick and sawed-off small samples. The following conclusions were reached: (1) testing the strength of the brick after the freezing test is to be recommended; (2) whole brick are more sensitive to freezing and thawing than small samples; and (3) an increase in the number of freezings from 25 to 50 decreases the strength still further but less than the first 25 cycles. W.K.

Effect of mode of manufacture on some physical properties of building brick. A. Green. *Brit. Clayworker*, **46** [549] 365–66 (1938).—Tests were made to ascertain what differences occurred in the more important physical properties of building brick manufactured from clays prepared in two ways, *viz.*, wet-ground and dry-ground, and the differences which occurred between handmade and machine-pressed brick of the two clays. The permeability results indicated that (1) brick made from the wet-ground clay were at first more permeable to water than brick made from dry-ground clay, but the latter tended to reach the saturation point quicker and had the higher permeability at the end of 24 hr.; and (2) at the commencement of the tests the wire-cut machine-pressed brick had higher permeabilities and reached the saturation point sooner than the handmade brick, and the final permeabilities were greater. The porosity figures showed that (*a*) brick made from dry-ground clay tended to have lower apparent porosities than wet-ground clay brick, and (*b*) wire-cut machine-pressed brick consistently gave higher porosity values than the handmade brick. The crushing strength figures indicated that (1) brick made from wet-ground clay had higher crushing strength values than brick made from the dry-ground clay, and (2) the wire-cut machine-pressed brick had lower crushing strengths than the handmade. Handmade brick showed superiority in all the tests over wire-cut machine-pressed brick. R.A.H.

Lightweight building materials with foamy structure. H Wolf and H. Welsch. Read before Verein der Chemiker, 48th Meeting, Königsberg, July, 1935; *Angew. Chem.*, **48**, 642–44 (1935).—Materials are discussed such as tuff, pumice, hollow brick, containing combustibles (lignite, etc.) in the hollow space, hydraulic building materials with added inflating substances (carbonates, metals, *e.g.*, aluminum, carbides), and gas concrete with special mention of the foamy building materials (foamy concrete made by the Iporite process of the I. G.). The λ values of Iporite concrete in comparison with other building materials are shown in a table. Foamy gypsum, brick, and calcium hydrosilicates, as well as foamy materials from synthetic resins, can be made in a similar manner. E.W.S.

New practice in rolling. Anon. *Dependable Highways*, No. 157, p. 3 (1937).—Rolling brick pavements on boards is a recent innovation that originated at Richmond, Va. It has several advantages over previous methods of rolling. The Richmond specifications for the practice of rolling on boards are quoted. P.S.D.

Queensland favors stoneware for sewerage pipe. Anon. *Clay Prod. Jour. Australia*, **5** [3] 4 (1938).—Every city and town in Queensland now constructing sewerage schemes is using stoneware pipe in all sizes within the limit of manufacture. Townsville, which had a contract for concrete pipes, cancelled this contract in favor of stoneware. It is predicted that, within 5 years, no concrete pipe will be used in any state in Australia for sewer purposes. H.H.S.

Reinforced brick pavement. Anon. *Dependable Highways*, No. 157, p. 5 (1937).—The construction of a test section of reinforced brick pavement, using large vitrified paving blocks, is briefly described. This type of pavement is said to require no curbs and no headers on the sides and is estimated to be less expensive to construct than the usual design. P.S.D.

PATENT

Building tile. A. C. Van Antwerp (Eastern Illinois Clay Co.). U. S. 2,108,396, Feb. 15, 1938 (Dec. 24, 1936).

Building tile comprises a plurality of blocks arrangeable end to end, the end portions of adjacent blocks being of irregular formation and coöperating to provide sinuous cavities or recesses between the blocks into which nails may be driven to attach a base strip or other member to a wall constructed of such tile, the form of such cavities or recesses causing the nails to be clinched and held against unintended loosening or pulling out.

Refractories

Acceptance and possibility of utilization of fireclay brick. R. RASCH. *Glückauf*, **73** [46] 1033–37 (1937).—R. gives the requirements for a good refractory brick. If the brick does not bind properly it is due to insufficient decomposition of the clay. Cracks usually do not impair the quality as they improve the resistance against temperature changes. Brick should never be brittle or contain striation; the latter is caused by air inclusion during manufacturing processes and is harmful. Waviness is due to disintegration of the mass of fire clay during forming. Remarks on general appearance are added. M.H.

Action of alkalis on refractory brick. F. HARTMANN. *Stahl & Eisen*, **57**, 1017–22 (1937).—An investigation of the effect of alkalis on refractory materials is necessitated by the increasing use of alkali-rich slags in foundry practice. A distinction is made between the action of alkali vapor, molten alkalis, and slags containing alkalis on refractory brickwork. Prisms of different refractory materials were heated in an electric furnace at temperatures up to 1200°C in the vapor arising from molten soda and also in that from the molten alkali. The matrix of silica brick was slightly changed by alkali vapor at moderate temperatures and the surface dissolved. Larger quartz grains were more resistant. Silica brick retained their shape and strength. Fireclay brick exposed to alkali vapor at 1000°C were soft at depth and were deformed slightly. In contact with liquid alkali, a glaze was formed on the surface of fireclay brick and the material swelled up. Magnesite proved to be durable to both types of attack. Chrome magnesite, on the other hand, was easily broken down throughout by the liquid and gaseous alkali, since the chrome ore was taken into solution by fusion. Bauxite brick, in spite of a higher alumina content, were warped by the treatment with alkali vapor. The structure was dissolved into an alkali-aluminum-silicate glass, and the volume of the piece increased considerably. The lining of plastic luting sand of a ladle was completely destroyed by molten soda through the formation of fissures. By using a luting sand of lower clay content the attack by soda was reduced. In the investigation of the attack of alkali-containing slags on magnesite for pig-iron mixers, it was found that additions of alkali to the slag caused correspondingly increased attack. The brick swelled up. This is true for slags rich in lime and silica. Slags containing more manganese and iron were made viscous by the addition of alkali and so were incapable of attacking the refractories. These results were confirmed by the measurement of the dependence of viscosity of such slags on temperature on the assumption that the most corrosive slags are the more liquid at a given temperature. Highly basic slags such as blast-furnace slags could not be made mobile by soda additions. In the discussion, an aluminous brick (38% Al_2O_3) of high density (8% porosity) was said to be the most resistant to molten alkalis and alkali-rich slags. By the addition of 5 to 10% graphite, the resistance could be increased L.R.B.

Actual manufacture and properties of refractory products. MARCEL LÉPINGLE. *Céramique*, **50** [596] 187–95 (1937).—L. visited a number of refractory works and presents the results of his observations. The methods of manufacture are functions of social and economic conditions; the criterion is the quality of the product and not the manufacturing method. The control of raw materials and laboratory analysis are necessary. Certain plants obtain good results by old methods The method of dry mixes, based on the principles of supercompression and peptizing of the clays, yields excellent results. Ramming is done by mechanical or pneumatic hammers. Present-day presses eliminate occluded air. The supercompression increases the density of the products without reducing their resistance to thermal shock. The chief advantage of the dry mix is the elimination of the risks of drying. The casting of Corhart type blocks is the ideal solution. Individual furnaces are used for all types of refractories; continuous furnaces are mainly used for silicoaluminous and extra-aluminous products. The white color of the refractory and its alumina content are not decisive criteria. Fluxes contained by the refractory are not as important as generally assumed. M.V.C.

Addition of coarse-grained sand to silica-brick mixes. I. S. SMELYANSKIĬ AND L. DRAZHNIKOVA. *Ogneupory*, **4** [8] 498–504 (1936); abstracted in *Referat. Silikatliteratur*, **4** [8] 4347 (1937).—Different sands of various grain size were added to quartzite mixes and their effect was studied. The best results were obtained with coarse-grained quartz sand from Pologi. M.V.C.

After-contraction test for fireclay brick. H. D. BENNIE. *Brit. Clayworker*, **46** [549] 370–71 (1938).—Because of the difficulty of accurately measuring after-contraction or expansion of refractory products, B. suggests the use of a mercury volumeter to determine such changes by volume rather than the use of calipers with which linear changes are obtained. The suggested mercury volumeter is described. R.A.H.

Bauxite: Séailles process for alumina. ANON. *Discovery*, **18** [213] 272 (1937).—The Séailles process is said to have an advantage over the Bayer process in that siliceous and low-grade bauxites may be used. A mixture of bauxite and limestone is calcined at 950 to 1100°C, a temperature at which the calcined product is friable, easily ground, and of maximum solubility in water. The crude Ca aluminate is treated with water and filtered; the filtrate is impregnated with CO_2 from the calcination, by which method Al_2O_3 and $CaCO_3$ are formed. Further saturation with CO_2 makes soluble Ca bicarbonate, the residue being Al_2O_3

with less than 1% of $CaCO_3$. See *Ceram. Abs.* **16** [6] 176 (1937). H.H.S.

Behavior of refractory materials under torsion at different temperatures: III—A, Modification to apparatus; B, Ultimate strength of kaolin and kaolin-quartz mixtures. A. L. ROBERTS AND J. W. COBB. *Brit. Clayworker*, **46** [550] 403–407 (1938).—The following modifications to the apparatus for making these tests, previously described, were made in order to extend the scope of the apparatus to the measurement of ultimate shear strength and to permit the use of a simple type of test piece: (1) a modified method of loading, by which the stress applied to the test piece may be increased continuously and uniformly and at different controlled rates; (2) a differential method of deflection measurement which enables the effective length of the test piece to be defined more accurately; and (3) new chucks with their design based on the universal joint, ensuring freedom from strain in test pieces when mounted and when subjected during the tests to purely torsional stresses. The results of ultimate shear strength and rigidity modulus measurements on fired test pieces of kaolin and quartzite are described. In heating from air temperature to 800°C, significant changes in the ultimate shear strength or rigidity modulus were absent in the kaolin, whereas with the kaolin-quartz the values of both these properties increased considerably and to the same extent. From 800° to 1100°C the development of plasticity in both materials was marked by a pronounced increase in the ratio of ultimate shear strength to rigidity modulus, the ultimate shear strength showing relatively little alteration while the rigidity modulus decreased markedly. For Part II see *Ceram. Abs.*, **16** [1] 20 (1937). R.A.H.

Chrome-ore raw materials for the refractory industry. N. M. FEDOROVSKIĬ. *Ogneupory*, **4**, 541–47 (1936); *Chem. Abs.*, **31**, 3655 (1937).—A description of the different Ural deposits is given.

Development of the magnesite works in Satka during the First Five-Year Plan. L. LOCH. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 350–61 (1937).—The magnesite deposits in this Western Ural mountain district are similar to the Styrian deposits but are not quite as finely crystalline as the latter and have a grayish white color. L. gives geological conditions, geographical distribution, mining and transportation methods, and production statistics and describes furnaces for the production of sinter and magnesite brick. The capacity of the plant is, at present, 80,000 tons per year. M.H.

Drying refractories for the glass industry. A. A. GEZBURG. *Keram. & Steklo*, **13** [11] 18–21 (1937).—Numerous experiments with the drying of refractories in artificial driers are discussed. Thirteen days are required to dry refractories in driers having an average temperature of 23°C after which they can be fired without danger of damage. The brick shrinks during the first 5 days of drying; only after this shrinkage is it possible to raise the temperature of the drying chambers. M.V.C.

Effect of coal ash on boiler refractories. ANON. *Eng. & Boiler House Rev.*, **51** [6] 404 (1937).—Damage to refractories is caused by (1) spalling due to the contraction of the solidified slag on the surface of the brick and (2) erosion due to molten slag. Use of a mixture of coals whose ash fusion temperatures vary widely may result in a very low fusing ash. In general, coals having an ash of high fusion temperature are preferred. B.C.R.

Effect of fluxes on the under-load strength of a fire clay. J. F. HYSLOP AND J. MCNAB. *Brit. Clayworker*, **46** [549] 373–76 (1938).—Additions of 5% of various oxides to a highly refractory fire clay show that (1) the fluxes act in the decreasing order MgO + CaO, Na_2O, Na_2O + CaO; MgO, mill scale + MgO, CaO; mill scale + CaO, mill scale + Na_2O; Na_2O + MgO, K_2O + MgO, mill scale; K_2O, Fe_2O_3, fayalite ($2FeO \cdot SiO_2$). (2) Separating these, the order for the straight oxides is Na_2O, MgO, CaO, mill scale, K_2O, Fe_2O_3, fayalite; and for the mixed oxides, MgO + CaO, Na_2O + CaO; mill scale + MgO; mill scale + CaO; mill scale + Na_2O; Na_2O + MgO; K_2O + MgO. (3) The average fluxing effect (the temperature at which there is 4% deformation under a load of 25 lb./in.^{2} for the mixtures 95% brick + 5% flux) is 1430°C, and the fluxes or slags which give this or a lower figure are powerful and energetic. R.A.H.

Essential properties of boiler refractories. ANON. *Eng. & Boiler House Rev.*, **50** [10] 667–70 (1937).—Porosity, resistance to slag penetration, spalling fusion temperature, and thermal expansion are considered the most important properties. The chemical composition of the fly ash impinging on the wall and the furnace atmosphere are important factors. The presence of FeO in slag and S in furnace gases has an important influence on the temperature of reaction between the slag and the refractory. Slags high in Ca, Mg, Fe, and alkalis have a lower fusion temperature and are more fluid than those containing greater amounts of SiO_2 and Al_2O_3. B.C.R

Extraction of alumina from highly aluminous raw materials. SHOICHIRO NAGAI AND JUNZO KATAYAMA. *Jour. Soc. Chem. Ind. Japan*, **40** [8] 302–303B (1937).—Results of studies on the extraction of alumina by the special semi-dry method are reported. M.V.C.

Heat-resistant magnesite. Z. YA. TABAKOV AND V. V. BELOVODSKIĬ. *Ogneupory*, **4** [5] 295–97 (1936).—The characteristics of the heat-resistant magnesite brick are refractoriness not less than 2000°C, mechanical strength from 450 to 500 kg./sq. cm., temperature of deformation under load from 1460° to 1520°C, and average thermal stability 25 to 30. M.V.C.

High alumina bodies—andalusite corundum refractories. S. A. LEVENSHTEIN. *Ogneupory*, **4** [6] 360–69 (1936).—L. describes in detail studies made by the Institute of Refractories dealing with the characteristics of andalusite corundum refractories and their manufacture. See *Ceram. Abs.*, **17** [2] 71, 72 (1938). M.V.C.

Highly refractory materials found in France. V. C. *Rev. Matériaux Construction Trav. Publics*, No. 336, pp. 136–38B (1937).—The deposits and characteristics of bauxite, sillimanite, corundum, zirconium, disthene, chromite, magnesite, beryllium, graphite, and olivine located in France are briefly discussed. M.V.C.

Hydraulic refractory cements: I-II. S. NAGAI. *Jour. Soc. Chem. Ind. Japan*, **40** [6] 197–98B; [12] 470–71B (1937).—Because of unsatisfactory results obtained with ordinary refractory cements composed of ground grog and raw refractory clay, experiments were made with special cements composed of ground diaspore or kyanite fired to

1500° or 1600° and mixed with limestone and slaked lime. The chemical composition of the samples was from 52.5 to 77.4 Al_2O_3, 10.8 to 35.3 SiO_2, 6.2 to 11.3 CaO, 2.0 to 3.3 TiO_2, and 1.4 to 2.5% Fe_2O_3. The softening point of the samples was from 1550° to 1650°. M.V.C.

Important properties of refractory materials. ANON. *Eng. & Boiler House Rev.*, **50**, 667–70 (1937); abstracted in *Sprechsaal*, **70** [25] 327 (1937).—The properties of refractory materials used in boilers are discussed. They depend on 3 groups of factors: (1) factors depending on the type of construction of the boiler, (2) kind of fuel and method of charging, and (3) conditions of operation. M.V.C.

Load-bearing ability of ceramic products at high temperature and a new method for testing it. SEIJI KONDO AND SHIN-ICHI SUZUKI. *Jour. Soc. Chem. Ind. Japan*, **40** [8] 282B (1937). M.V.C.

Magnesia brick. R. LEDUC. *Rev. Matériaux Construction Trav. Publics*, No. 334, p. 106B (1937).—By means of special methods, magnesia brick with a low iron content which do not color glass melts and which resist variations of temperature well were produced. The great advantage of such brick when used as linings in tank furnaces lies in the fact that they possess a high density, thus preventing the soiling of the glass by the refractory which sometimes happens when aluminous or silicoaluminous brick are used. Magnesia brick with a low iron content can also be used for burners of tank furnaces because they are thermally resistant. Magnesia and silica brick react when in contact; therefore an intermediate layer of chrome brick whose neutrality prevents the reaction of basic brick and acid brick is recommended. For tank furnaces, mullite, sillimanite, or corundum brick are preferable for an intermediate layer to prevent the coloring of molten glass by chrome. M.V.C.

Method for producing fireproof substances by improving raw materials by extremely high temperatures. RUDOLF SCHNABEL. *Chem. Fabrik*, **1937**, p. 436; *Chem. Abs.*, **32**, 741 (1938).—The density of the raw ceramic materials is greatly increased by the Schnabel-Bone process of flameless surface combustion, by which temperatures approaching those of the electric furnace are attained.

Monofrax refractories. A. PAUL THOMPSON. *Glass Ind.*, **18** [11] 363–66 (1937).—Monofrax is the term designating a series of new super-refractory materials made by casting electric furnace fused material into shapes. As attack on refractories occurs not only on the surface but also in the pores, dissolving the bond, it is obvious that using a homogeneous casting of the more resistant material is the solution to the problem. Petrographic studies having revealed that alpha alumina was the most stable phase occurring at the interface of glass and refractory after a flux block of clay or other type had been in use for a long period of time, a great deal of study was devoted to the problem of converting this material into a form most suitable for glass tank use. As various types of glass would react on the refractories in different ways, a series of different refractories was developed. Actual service tests were made on samples of the cast refractory mixes using (*a*) a high soda-lime glass containing somewhat more alkali than usual; (*b*) a borosilicate glass; and (*c*) an opal or fluoride glass, exposing the blocks to "half-immersion" for 100 hr. Careful evaluation of the results obtained led to a more selected group of samples for large-scale tests. Preferred mixes fall into three general groups as follows: (1) Monofrax L, (2) Monofrax H, and (3) Monofrax K ("Refractory—," *Ceram. Abs.*, **17** [4] 145 (1938)). The casting temperatures of the preferred Monofrax mixes vary from 3300° to 3800°F. All the mixes possess unusual refractoriness and have a high load-bearing capacity at elevated temperatures; their coefficient of expansion is quite moderate. E.J.V.

Physical properties of some South African raw materials for silica brick. V. L. BOSAZZA. *Jour. Chem. Met. Mining Soc. S. Africa*, **37** [12] 590–94 (1937).—B. cites his earlier work on chemical and mineralogical properties, and, from combined investigations, establishes the order of merit of various classes of material. The physical properties in order of importance are (1) condition and size of crystal grain, (2) porosities in raw and fired states, (3) shape of particle on crushing, and (4) rate of inversion on heating to 1470° to 1500°C. **Discussion.** *Ibid.*, **38** [2] 72–73 (1937). E.H.McC.

Production of high temperatures. E. LAX AND M. SCHÖN. *Chem. App.* **24** [22] 361–63; [24] 393–95 (1937).—The highest temperatures required for technical processes do not exceed 4000°C as at this temperature all matter, even that with the highest melting point, liquefies. A permanent temperature of 8000° can be produced in the electric arc and one of 15,000° in the Hg arc. A table of melting points for materials is given; 3550° ± 30 for C is maximum. The material in which the substance can be heated is mentioned. Another table gives the melting points of materials for refractories:

Hafnium carbide	3890 ± 100	Hafnium boride	3065 ± 50
Tantalum "	3880 ± 100	Thorium oxide	>3000
Zirconium "	3530 ± 100	Zirconium boride	2990 ± 50
Niobium "	3500 ± 100	Zirconium nitride	2980 ± 50
Hafnium nitride	3310 ± 100	Titanium nitride	2950 ± 50
Titanium carbide	3140 ± 90	Tungsten boride	2920 ± 50
Tantalum nitride	3090 ± 50	Tungsten carbide	2870 ± 50

Some of these materials can be heated only in a vacuum or in a protective atmosphere because of their tendency to oxidize or combine with other gases at high temperatures. Specific heat and conductivity of gases, electric energy required for heating, flame temperatures, heat of formation, and thermite reactions (with metal powders) are discussed. M.H.

Quantitative relationship of clay and grog in sagger mixes. R. MAKHL. *Keram. & Steklo*, **13** [11] 29–32 (1937).—A great number of factors affect the characteristics of sagger mixes. In general, the change of properties of lean and fat mixes, used for saggers, proceeds according to the same principle. The basic conclusion is that the increase of the clay content of sagger mixes affects their properties favorably and that a greater clay content should be used in saggers which do not require high thermal stability in operation. M.V.C.

Regenerative furnace refractories. DONALD ROSS. *Glass Ind.*, **18** [7] 241–43 (1937).—Efficiencies in checkers are affected both by construction and by the physical and chemical properties of the checker materials. Principal sections through the heat-absorbing checkers should be thin enough so that the temperature of their centers will

vary sufficiently during a cycle to perform useful service. The mass of heat-absorbing material per unit of checker chamber space should be as great as possible and still permit suitable flue space for efficient heating of the checkers. Checker tile should be of material that will not shrink in use. Dense checker tile have advantages over porous tile. Silica brick used as checkers do not shrink in use, stand rigidly in place until the end of the fire, and wash clean so that checkers made of them are not apt to clog if run sufficiently hot, but if run hot they are fluxed away rapidly by basic dust and vapors. Siliceous fireclay brick of low flux content do not shrink appreciably and tend to remain clean. Low porosity alumina checker tile will not shrink. Items of attack chiefly responsible for the destruction of the tank block are (1) attack on vertical faces of tank blocks below the metal line, not excessively rapid if the structure of the block is mechanically good; (2) attack at the metal line, at present the limiting factor in the life of most tanks; (3) upward eating of downward facing surfaces, commonly rapid and destructive; and (4) destruction of downward facing surfaces of flow holes or "throats" between melting and refining compartments; like metal line attack this is one of the chief causes of failure of tanks. After discussing the refractories now being used for the various services enumerated, R. suggests as a possible future refractory for all of these services a high-magnesia or periclase block which is very refractory and relatively inert. E.J.V.

Relationship between structure and life of silica brick in the roof of an open-hearth steel furnace. V. L. Bosazza. *Jour. Chem. Met. Mining Soc. S. Africa*, **37** [10] 526–32 (1937).—Examination of South African, American, English, and German brick reveals wide variation in structure and texture. Microscopic examination indicates that slag attack is influenced by the fineness and packing of the particles and by the porosity and nature of the pores. Low porosity and low permeability depend largely on these properties in the raw material. Particles should be angular to subangular in shape and so packed that interlocking occurs. Titanium oxide is thought to have an inhibiting effect on the inversion of upper high or beta 2 tridymite to high or beta cristobalite. **Discussion.** *Ibid.*, [12] 586–88; **38** [2] 74–75 (1937). E.H.McC.

Reliability of thermal conductivity measurements for insulating materials. H. Oliver. *Brit. Clayworker*, **46** [550] 409–12 (1938).—Samples of practically identical diatomaceous insulating materials were tested for thermal conductivity by three independent authorities, and the results were compared with those obtained by O. on the same brick. A reasonable degree of concordance in results may be obtained by a particular apparatus. Discrepancies are liable to occur between the results reported by different laboratories of an order which is in some instances considerably greater than that covering the limits of reproduction of an apparatus. This indicates that some tolerance should be used when making comparisons of the relative insulating efficiency of samples of this class of material from the thermal conductivity values. R.A.H.

Resistance of grog bodies to the attack of molten glass. K. G. Kumanin. *Optiko-Mekh. Prom.*, **7** [5] 6–7 (1937); abstracted in *Chem. Zentr.*, **1937**, ii, 4222.—From 0.6 to 1.2% CoO, as $Co(NO_3)_2$, was added to the grog mix. After firing, the samples were immersed in molten glass. Because of the disintegration of grog, CoO contaminated the glass melt; the color tone of the glass yie ds the extent of attack. M.V.C.

Results obtained with chrome-magnesite brick in open-hearth steel furnaces. A. E. Dodd. *Brit. Clayworker*, **46** [550] 408–409 (1938).—The gas ports and blocks of a 70-ton furnace were built of brick having the following composition: SiO_2 4.8, Al_2O_3 2.8, Fe_2O_3 11.5, Cr_2O_3 34.8, CaO 2.0, MgO 39.2%. During the second week of working, disintegration of the brick had become so bad that it became necessary to clean the gas slopes after each heating. This cleaning consumed 8 man-hr. per day. It is hypothesized that under alternately oxidizing and reducing conditions the "iron" may continuously alternate between the di- and the tri-valent forms. The disintegration of the brick (flaking) would then be caused by the expanding and the contracting of the complex spinel crystals which are present in the brick with the changing of the iron from one state to another. In a second trial, parts of the air uptakes of a 200-ton tilting furnace were lined with brick of a similar type but of slightly different composition. These brick also flaked at the working face in layers of about 1/4 in. and alternate light and dark bands had formed within the brick. The zones outlined by these bands are possibly due to the absorption and migration of slag and impurities which may be the cause of spalling and differences in thermal expansion. R.A.H.

Selecting the proper refractory for hot-zone linings of kilns. C. H. Sonntag. *Rock Products*, **41** [2] 52–53 (1938).—The principal reason for failure of a hot-zone lining in a cement kiln is the fluxing action occurring between the clinker and the lining. Since clinker is chemically basic, it should, while at its temperature of formation, be in contact with a basic refractory. Use of 70% alumina brick has resulted in improved service where conditions are not too severe. The only commercially available truly basic lining consists essentially of magnesite brick. Their use in the first rotary cement kiln in which they were tried showed their life exceeded by over seven times that of 70% alumina brick that were previously used. Petrographic study of the transition zone between brick and clinker shows a zone about 1 in. thick in the case of 70% alumina brick, with a progressive change from the unaltered brick to the clinker. In this zone a layer was found which has a melting point of about 300°F below the usual operating temperature of a cement kiln, and the only reasons why this layer remains solid are the protection afforded by the coating and the heat conduction outward through the brick and kiln shell. No such reaction zone is found between clinker and magnesite brick. The change from clinker to brick is abrupt, and there is little evidence of chemical action between them. No layer has been found whose fusion point is not far higher than the operating temperature of the kiln. In selecting linings for lime kilns one must look for lack of slag formation, spalling resistance, and ability to withstand the abrasive action of the lime as it moves down the kiln. E.J.V.

Siemensite and its use in basic open-hearth furnace. E. Greiner. *Rev. Universelle Mines*, **11** [13] 502–506 (1935).—G. gives a treatise on the results of tests made since 1928 with siemensite, which is distinguished by its

great resistance to high temperatures in connection with the construction of Martin furnaces. He supplemented the results by those recently obtained at the Société Cockerill with a view to an important reduction in the consumption of refractory materials coupled with an increase in the productive capacity of the furnaces. Photographs and tables are given. E.W.S.

Simplified calculation of recuperators and regenerators. KURT RUMMEL AND FRITZ KESSLER. *Arch. Eisenhüttenwesen*, **10**, 233–42 (1936); *Chem. Abs.*, **31**, 7706 (1937).—A simplified method for both new design and checking or redesigning existing installations for recuperating waste heat is explained. Diagrams, nomograms, and tables are given for coefficients of heat transmission, conduction, and utilization of material. The method is illustrated by a few examples.

Studies and experiments with refractory materials at the Spetzstal plants. A. T. JACQUES. *Kachestvennaya Stal*, **4** [5] 58–59 (1936); abstracted in *Referat. Silikatliteratur*, **4** [10] 4595 (1937).—Grog spouts were replaced by magnesite spouts at the special steel plant of Krasny Oktyabr with good results. Good results were also obtained with spouts and plugs made from refractory clay containing iron and titanium, using grog having larger grains. M.V.C.

Tank block testing. OTTO BARTSCH. *Glastech. Ber.*, **15** [9] 353–59 (1937).—With improving resistance to corrosion of tank blocks it is necessary to broaden the scope of usual tests because of resultant glass flaws (streaks and stones). Besides solubility, the course of the solution process, including profile, nature of surface, and effect on glass quality, should be known. The three usual methods (model tank, immersion, and floating body) were found suitable for solubility, but not for estimating the tendency to streak or stone formation. Changes in the $SiO_2 : Al_2O_3$ ratio of the refractory after treatment with fused soda or sulfate has possibilities for estimating stone formation. Other factors such as determination of pore structure are also important. The Osram procedure for streaks gives results in agreement with practice. This consists of treating a refractory test piece with batch at 1400°C, pouring the glass into slabs, polishing, photographing in parallel light, and comparing. In special cases a test block can be floated in a forehearth and the glass compared with glass from a forehearth under otherwise identical conditions. J.F.H.

Thermal conductivity under special environmental conditions. GINO BOZZA. *Rend. ist. lombardo sci.*, **68**, 608–18 (1935); *Chem. Zentr.*, **1936**, ii, 436; *Chem. Abs.*, **31**, 7735 (1937).—The cooling of a plane plate was studied under such conditions that the heat transfer took place through convection and radiation. From the mathematical theory of heat transfer a special radiation coefficient and a special mean temperature of the environment are defined, both of which change with the surface temperature. Expressions are given that permit calculation of the temperature variation in the plate and the time in which the two parameters can be regarded as constant. Suitable changes are given for the expression for cases in which shorter time intervals are chosen.

Use of a spinel binder for chromite refractories. V. GONCHAROV, K. FEODOT'EV, AND D. VOGMAN. *Ogneupory*, **4**, 552–53 (1936); *Chem. Abs.*, **31**, 3655 (1937).—With 10 to 20% of a spinel binder obtained by adding fused magnesite and Al_2O_3 to the batch, a highly refractory (over 1920°) material, resistant to deformation under load (beginning at 1730°), was obtained under laboratory conditions.

PATENTS

Brick for the roof of glass furnaces. N. V. OSTRIKOV. Russ. 42,853, April 30, 1935; *Chem. Abs.*, **31**, 7616 (1937). The brick are successively treated with a strong solution of water glass, HCl, and water before firing.

Ceramic material. VICTOR MORITZ GOLDSCHMIDT. Fr. 811,237, April 9, 1937; *Chem. Abs.*, **32**, 743 (1938).—A ceramic material is made from a mixture of coarse and fine grains. The coarse grains are composed of Mg orthosilicate or substances rich in it, *e.g.*, olivine ores, while the fine grains are composed of refractory material of other kinds and of greater dispersion, particularly MgO of coarse crystalline structure, *e.g.*, magnesite of concretion or calcined magnesite, or (and) compounds containing Cr, *e.g.*, Cr_2O_3 or siderochrome.

Ceramic objects. COMPAGNIE DES MEULES NORTON (SOC. ANON.). Fr. 812,189, May 1, 1937; *Chem. Abs.*, **32**, 743 (1938).—Refractory objects are made from a mixture containing a substance reacting readily with O, a vitrifiable substance, carbide of Si and B or diamond powder and Al, Si, Mg, or carbide or lower oxide of B. Thus, the mixture may contain borax, B_2O_3, SiO_2, $Al(OH)_3$, $CaCO_3$, pulverized Al or Si, potter's clay, and diamond powder.

Checker-brick assemblies for furnace regenerators. OPEN HEARTH COMBUSTION CO. Brit. 479,125, Feb. 16, 1938 (March 2, 1936).

Checker-brick construction. G. L. DANFORTH, JR. (Open-Hearth Combustion Co.) Can. 371,329, Jan. 18, 1938 (Aug. 4, 1936); see *Ceram. Abs.*, **16** [11] 341 (1937). G.M.H.

Checkerwork. H. L. SMALLEY (Harbison-Walker Refractories Co.). U. S. 2,108,871, Feb. 22, 1938 (May 26, 1937).

Crystalline cast refractory articles and their production. W. J. TENNANT (Carborundum Co.). Brit. 480,256, March 2, 1938 (Aug. 18, 1936).

Ferruginous siliceous refractories. J. M. MCKINLEY (North American Refractories Co.) AND W. K. CARTER (National Aluminate Corp.). U. S. 2,108,543, Feb. 15, 1938 (July 3, 1935). A fired ceramic product comprises siliceous particles and barium ferrite.

Furnace brick. E. H. SANCTON AND D. W. STEWART (Canadian Refractories, Ltd.). Can. 371,616, Feb. 1, 1938 (Aug. 12, 1936). G.M.H.

Furnace-roof brick. E. H. SANCTON AND D. W. STEWART (Canadian Refractories, Ltd.). Can. 371,615, Feb. 1, 1938 (Aug. 12, 1936). G.M.H.

Furnace wall construction. L. H. HOSBEIN (M. H. Detrick Co.). U. S. 2,110,419, March 8, 1938 (June 24, 1936).

Furnace walls. BABCOCK & WILCOX, LTD. Brit. 478,784, Feb. 9, 1938 (June 24, 1936).

Lime-resistant refractory. H. C. LEE (Basic Dolomite, Inc.). Can. 371,285, Jan. 18, 1938 (May 8, 1936; in U. S., Sept. 16, 1935). G.M.H.

Metallurgical furnace masonry. ÖSTERREICHISCH AMERIKANISCHE MAGNESIT A.-G. (Josef Berlek, inventor).

Austrian 150,288, July 26, 1937; Cl. 40*a*; *Chem. Abs.*, **31**, 7211 (1937).—An improvement is described in the known method of uniting refractory brick by means of interposed sheet-metal layers which are afterward fused.

Refractory brick. MAGNESIT-INDUSTRIE A.-G. Austrian 150,622, Sept. 10, 1937; Cl. 80*d*; *Chem. Abs.*, **32**, 1067 (1938).—Brick which are stable to temperature variations are made from a mixture containing (*a*) powdered magnesite and (*b*) coarse granules of a variety of magnesite containing Fe_2O_3 in a proportion 2 to 4% greater than the proportion of Fe_2O_3 in the powdered magnesite. Component (*b*) of the mixture may include also Cr ore in a proportion of 6 to 30%, calculated on the whole mixture.

Refractory cement. N. V. OSTRIKOV. Russ. 42,851, April 30, 1935; *Chem. Abs.*, **31**, 7616 (1937).—Glass furnaces are cemented with a mixture of disintegrated graphite, talc, and refractory clay.

Refractory material. CARBORUNDUM CO. Ger. 651,994, Oct. 23, 1937; Cl. 80*b*. 8.09; *Chem. Abs.*, **32**, 744 (1938).—Fireproof masses are produced by molding a fused mixture of 2 to 10% MgO and 90 to 98% Al_2O_3.

Refractory material. A. A. FOWLER AND R. M. OTIS. Can. 371,701, Feb. 1, 1938 (April 17, 1936). G.M.H.

Refractory materials. COMPAGNIE DES MEULES NORTON (SOC. ANON.). Fr. 812,193, May 1, 1937; *Chem. Abs.*, **32**, 744 (1938).—Apparatus is described for making refractory masses by subjecting pulverized refractory metal oxides to pressure at a temperature at which the mass is plastic. Oxides of Al, Mg, Si, Zr, Ti, Be, Th, Ce, and Cr may be used.

Refractory materials. VICTOR M. GOLDSCHMIDT. Ger. 650,717, Sept. 30, 1937; Cl. 80*b*. 8.08; *Chem. Abs.*, **32**, 1066 (1938). Addition to Ger. 605,371 (*Ceram. Abs.*, **14** [6] 143 (1935)).—Finely granular natural or synthetic ferruginous material containing Mg orthosilicate is mixed with sintered MgO in powdered or finely granular form, and the mixture is heated to a temperature below its melting point, *e.g.*, to 1300°. The mixture may first be molded, if desired, with the aid of a binder. The ferruginous starting material may contain also Mg hydro- and meta-silicates, and in this case it is preferably sintered at about 900° before it is mixed with the MgO. The latter may be taken in a sufficient excess to yield final products containing free MgO. Examples are given.

Refractory materials. VICTOR M. GOLDSCHMIDT. Fr. 811,659, April 20, 1937; *Chem. Abs.*, **32**, 744 (1938).—These are made by heating mixtures containing serpentine or crude materials rich in serpentine and materials rich in Mg, *e.g.*, MgO or substances capable of forming MgO. The powdered mixture is heated in a rotary furnace to a temperature suitable for the formation of Mg orthosilicate, and the calcined material is ground to the degree of granulation suitable for the formation of refractory products.

Refractory materials. W. SCHUMACHER. Ger. 651,788, Oct. 20, 1937; Cl. 80*b*. 1.02; *Chem. Abs.*, **32**, 744 (1938).—A bidding agent for powdered or granular minerals consists of finely ground CaO or MgO or substances containing these and finely ground siderite ($FeCO_3$) mixed to a paste with water. If freshly calcined lime is used for the CaO its quenching should be delayed as long as possible. Lightly clinkered dolomite or cement may be used for the CaO. Gypsum may be added to delay quenching of the CaO.

Refractory materials. UNION CARBIDE & CARBON RESEARCH LABORATORIES, INC. Fr. 813,692, June 7, 1937; *Chem. Abs.*, **32**, 1066 (1938).—Refractories such as those containing quartzite are made more stable to heat by grinding them and passing the ground product through a zone heated to 1500°. To the ground refractory is added an accelerator comprising 1 or more halides or silicohalides of alkali or alkaline-earth metals, *e.g.*, a mixture of K_2SiF_6 and SrF_2. An ester of silicic acid and an aliphatic alcohol which causes deposition of SiO_2 after hydrolysis are used as binder.

Refractory materials and articles. PILKINGTON BROS., LTD. Fr. 810,671 to 810,673, March 26, 1937; *Chem. Abs.*, **32**, 744 (1938).—Refractory articles composed of crystals buried in a vitreous gangue, the crystals being only of corundum, are made by adding a difficultly soluble substance containing F (fluorspar, cryolite, lepidolite, MgF_2, opal glass, or Na_2SiF_6) to a mixture composed of Al_2O_3 and SiO_2 (and (or) their compounds), a part of the components being in the plastic state, forming the articles, and heating them to below 1770°. The ratio of Al_2O_3 to SiO_2 and the amount of F compound are sufficiently high and the temperature is sufficiently low to insure the complete absence of mullite in the articles after firing.

Refractory products. GILBERT E. SEIL. Fr. 811,670, April 20, 1937; *Chem. Abs.*, **32**, 745 (1938).—A refractory product having a high softening point is made from natural chrome ore by subjecting the ore to a heat treatment in the presence of a Mg salt to a temperature at least equal to the firing temperature of the refractory. The salt is present in amount sufficient to furnish the MgO necessary to transform the whole or greater part of the gangue of low freezing point into forsterite but insufficient to decompose the spinel of the ore.

Terra Cotta

British modern architecture. GUNN GWENNET. *Clarté*, **10** [10] 7–11 (1937).—A collection of original pictures displayed at the Royal Academy of Arts, in London, represents edifices erected from 1900 to 1936, showing the evolution of British architecture. R.W.D.

Glazing, engobing, and "smoking" of roof tile. E. SCHONDORFF. *Tonind.-Ztg.*, **61** [53] 585–87; [54] 599–601; [55] 609–12 (1937).—S. discusses the following subjects: (1) general characteristics of glazes, engobes, and smoked tile, (2) relation of wave-length of light to the appearance of glazes, engobes, and smoked tile, (3) reflection of light and gloss, (4) white glazes and engobes, (5) gray coloring, especially that of smoked tile, (6) colors of glazes and engobes, (7) opacity, (8) choice of coloring agents for glazes and engobes, and (9) preparation of glazes and engobes. While restricted to brick and roof tile, the subject is discussed on a broad basis, showing the relationship between the length of light waves, the reflection and absorption of light, and difference between the index of refraction and the particle size and thickness of the slip on the one side and the color and texture of glazes and engobes on the other side. With the help of photomicrographs, S. shows

the proper preparation and application of glazes and engobes to insure a good bond with the body during the firing and drying processes. W.K.

Manufacture of salt-glazed stoneware pipes and fittings. A. COULHON. *Rev. Matériaux Construction Trav. Publics*, No. 329, pp. 26–29B; No. 330, pp. 42–45B; No. 331, pp. 58–62B; No. 333, pp. 88–93B; No. 334, pp. 100–102B; No. 335, pp. 118–22B; No. 336, pp. 130–34B (1937); see *Ceram. Abs.*, **17** [2] 76 (1938). M.V.C.

Manufacture of stoneware and concrete pipes and their uses. CYRIL POOLE. *Jour. Inst. Sanitary Engrs.*, **39**, 169–74 (1935); *Chem. Abs.*, **31**, 8854–55 (1937).—P. describes constructions for conduits.

Prevention of cracking of stoneware and unglazed ware. M. *Sprechsaal*, **69** [49] 723 (1936).—The method consists in applying, with a brush, a warm saturated soda solution over the edges of the ware or any other place where cracks or fissures may be expected. M.V.C.

Stability and protection of ceramic material in the construction of chemical equipment. W. STEGER. *Chem. Fabrik*, **1937**, pp. 394–96; *Chem. Abs.*, **31**, 8854 (1937).—The only real protection is a well-fired resistant glaze.

PATENTS

Porous ceramic ware. M. N. GENZLER. Russ. 43,831, July 31, 1935; *Chem. Abs.*, **31**, 7616 (1937).—To a frothed clay solution is gradually added dry powdered clay. The product is agitated, molded, dried, and fired in the usual manner.

Weatherproof masonry joint. F. P. WHITE. U. S. 2,108,358, Feb. 15, 1938 (Oct. 19, 1936). A masonry structure comprises a plurality of masonry units, laid in substantially horizontal courses connected by horizontal and vertical joints of binding material, the weather facing masonry units forming extended cavities from the binding material outward to the weather-exposed face of the structure, the cavities being filled by joint sealing members constructed of impenetrable springy material in a tubular form compressed between the extended masonry units to flex in response to the expansion and contraction of the structure.

Whiteware

Determining the elimination of water in slips by means of filtration analysis. V. V. GLASSON AND E. A. USPENSKAYA. *Keram. & Steklo*, **13** [11] 26–29 (1937).—The filtration analysis developed by W. Ostwald, A. Steiner, and W. Rath (*Kolloid-Z.*, **31**, 204 (1922); **33**, 109 (1924); **36**, 46 (1925)) was used for determining the amount of water eliminated by slips used for casting ware. This method permits the characterization of slips by determining the speed and time with which water is eliminated, amount of water separated, and moisture content of the body after casting; it is also possible to judge the degree of saturation of the slip with electrolyte and hence to control its quantity. The filtrate may be investigated with respect to its alkalinity by titration or by determining the p_H by means of the electrometric or colorimetric method. M.V.C.

Talc porcelain: IX–XII. SEIJI KONDO AND SHIN-ICHI SUZUKI. *Jour. Soc. Chem. Ind. Japan*, **40** [12] 468–70B (1937).—The authors studied (1) the effect of various gases on the firing behavior of talc, (2) physical properties of talc and talc porcelain, (3) BaO and quartz bodies, and (4) specific electrical resistance of porcelain composed of alkaline earths, alumina, and silica. For Parts **V–VIII** see *Ceram. Abs.*, **16** [11] 344 (1937). M.V.C.

PATENTS

Artificial teeth manufacture. E. L. PILKINGTON AND J. F. TURNER. Can. 371,541, Jan. 25, 1938 (Feb. 19, 1937). G.M.H.

Ceramic bodies, in particular for use as insulators for spark plugs. GENERAL MOTORS CORP. Brit. 479,124, Feb. 16, 1938 (June 27, 1935).

Ceramic body. A. H. FESSLER AND KARL SCHWARTZWALDER (General Motors Corp.). Can. 371,807, Feb. 8, 1938 (June 15, 1936; in U. S., June 27, 1935). G.M.H.

Ceramic insulator and method of making. L. R. SHARDLOW (Radio Corporation of America). U. S. 2,108,513, Feb. 15, 1938 (June 10, 1936). The method of making a porous ceramic insulator with a modulus of rupture of about 13,000 lb./ sq. in. for use at high voltages and high radio frequencies comprises mixing substantially pure alumina particles measuring about 2 microns in diameter with 4 to 8% powdered silica and 2 to 6% powdered acid magnesium metasilicate, pressing the particles under high pressure into intimate contact, and firing in a hydrogen atmosphere at about 1600°C for a period of about 140 sec.

Ceramic material. STEATIT-MAGNESIA AKT.-GES. Brit. 478,794, Feb. 9, 1938 (June 8, 1936).

Ceramic product manufacture. T. G. McDOUGAL (General Motors Corp.). Can. 371,808, Feb. 8, 1938 (June 15, 1936); see *Ceram. Abs.*, **16** [11] 347 (1937). G.M.H.

Clay. ROBERT LÖSSNITZ. Ger. 650,748, Sept. 30, 1937; Cl. 80*b*. 12.12; *Chem. Abs.*, **32**, 743 (1938).—The disruptive action of pieces of lime present in potter's clay is prevented by adding chloride to the clay before molding and firing. Chlorides of alkali metals, Fe, Ca, Al, Mg, and NH_4 may be used.

Defecator with integral tank and integral evacuator. W. C. GROENIGER (J. B. Pierce Foundation). U. S. 2,110,361, March 8, 1938 (April 30, 1936).

Dielectric material. NICOLAI P. BOGORODITSKIĬ AND NICOLAI V. TITOV. Fr. 814,744, June 28, 1937; *Chem. Abs.*, **32**, 1066 (1938).—A ceramic dielectric material, particularly for condensers, is composed essentially of Pb titanates. It may be made by mixing TiO_2 85 to 95 and PbO 15 to 16%, compressing, and heating to 1100° to 1180°.

Heat-resisting insulating material. GENERAL MOTORS CORP. Fr. 815,112, July 6, 1937; *Chem. Abs.*, **32**, 1421 (1938).—Insulating material for making spark plugs consists of a dense nonporous mass of Zr silicate mixed with one or more of the following substances, Al_2O_3, corundum, vitrified Zr, and small amounts of ZrO or Zr.

Joining ceramic articles and metals. RUDOLF SCHARFNAGEL. Fr. 810,388, March 20, 1937; *Chem. Abs.*, **32**, 743 (1938).—An alloy of relatively high melting point is placed between the ceramic article and the metal and the joint heated until the alloy melts. Examples of alloys

contain Ag 65, Cu 25, and Fe 10%, Cu 80, Ag 15, and Be 5%, or a Ag-Cu-Cd alloy containing 2 to 25% of Cd.

Spark plugs for internal-combustion engines. M. DELATTRE. Brit. 478,929, Feb. 9, 1938 (April 30, 1937). B. HOPPS AND A. M. LODGE. Brit. 478,761, Feb. 9, 1938 (Nov. 6, 1936).

Equipment and Apparatus

Apparatus for maintaining constant humidity. E. GRIFFITHS AND J. H. AWBERY. *Brit. Assn. Advancement Sci., Rept.*, **1936**, 324; abstracted in *Nat. Phys. Lab. Abs. Papers*, **1936**, 5.—Two forms of apparatus for (1) supplying a stream of air of known constant humidity, and (2) maintaining a chamber at a fixed humidity have been devised. In the former, separate streams of dry and saturated air are mixed to give the desired dew point; in the latter, a piece of goldbeater's skin controls, by its changing length with alteration of humidity in the chamber, fans which blow in dry or wet air. L.R.B.

Apparatus for testing crushing strength of granules. E. F. HARFORD. *Ind. Eng. Chem., Anal. Ed.*, **10** [1] 40–41 (1938).—A simple compression tester which combines speed, convenience, and reproducibility in the evaluation of granule characteristics is described and illustrated. F.G.H.

Applications of natural-color photography in mineralogy. B. M. SHAUB. *Amer. Mineralogist*, **23** [1] 20–27 (1938).—S. describes the necessary apparatus and procedure technique for making natural-color photographic exposures, prints, and transparencies of mineralogical specimens and points out the advantage of their use by the lecturer, student, and teacher. F.J.Z.

Applications of nickel alloy in the glass industry. ANON, *Glass Ind.*, **18** [10] 340–42 (1937).—Heat-resisting nickel alloys available for service in certain vital parts of glassmaking equipment may be divided into the following groups: (1) Cast irons containing up to 3% nickel, with or without chromium. Their heat-resisting properties are superior to those of ordinary cast iron, but they can not be compared with those of the true heat-resisting alloys. (2) High-alloy cast irons such as "Ni-Resist" and "Nicrosilal," containing up to 20% nickel. These alloys are austenitic in structure and have a high resistance to oxidation and growth, but are not generally suitable for temperatures above 800°C (1472°F), their strength being low even at this temperature. (3) Wrought and cast heat-resisting steels containing up to 36% nickel and 30% chromium, with or without additions of silicon, tungsten, etc. This group can be used, under suitable conditions, at temperatures up to 1050°C (1922°F) and is regularly employed for a wide range of high-temperature work. (4) Nickel-chromium and nickel-chromium-iron alloys containing high percentages of nickel, with or without other alloy additions. This group probably offers the best combination of properties at high temperatures. The choice of the most suitable alloy for any piece of glassmaking equipment depends upon local requirements. Applications of alloys for melting, working, and annealing equipment are discussed. E.J.V.

Automatic control and the chemical industries. LUIS DE FLOREZ. *Ind. Eng. Chem.*, **29** [11] 1210–13 (1937).—Successful automatic control can be judged only by improved results. The mere feat of maintaining some variable condition constant or of making it follow some given path is of no service to the industry unless the control of this variable proves to be a governing factor in improving industrial results. Illustrated. F.G.H.

Behavior of certain dusts under mechanical impingement. J. B. FICKLEN AND L. L. GOOLDEN. *Science*, [N.S.] **85** [2216] 587–88 (1937).—A brief study of breakage of dust particles by impact is given. The three dusts examined are quartz, orthoclase feldspar, and dried spores of *Pencillium oxalicum*. With two of the dusts, any estimation of particle-size distribution in the air from the resultant particles is erroneous. With each of the dusts, an estimation, under the observed conditions, of the number of particles in the air sampled is erroneous. E.H.McC.

Care of transmission belts. R. KOLLER. *Tonind.-Ztg.*, **61** [56] 623 (1937).—The proper care of belts in seasonal plants is stressed. Washing with soda solution and dressing with horse tallow or whale oil are recommended. During the off-season, the belts should be packed in wood shavings and kept in storage. W.K.

Centrifugal pumps for sludge and waste water. R. DZIALLAS. *Eng. Progress*, **18** [12] 274–76 (1937).—D. describes in detail several types of rotary pumps for pumping liquids carrying large amounts of solid material. 10 illustrations. J.L.G.

Continuous control systems with variable characteristics. H. M. SCHMITT. *Ind. Eng. Chem.*, **29** [11] 1229–31 (1937).—Three automatic control systems are described. Two are particularly applicable to electrical methods of temperature measurement and control in which thermocouples, resistance thermometers, or photoelectric cells are used as the measuring element, and motor-operated valves are employed to regulate the controlled medium. The third covers a pneumatic method for regulating the controlled medium in response to changes in temperature, pressure, flow, or liquid level. All three systems incorporate means for adjusting the throttling range and rate of automatic reset while the instruments are in operation. These characteristics result in automatic control systems adaptable to processes different in nature and operating conditions. Illustrated. F.G.H.

Cutting compressed air costs. ANON. *Glass Ind.*, **18** [10] 337–38 (1937).—The cost of compressed air is a recognizable item in the operating budget of a glass plant, and the compressor operator should consider the factors that prevent the compressor plant from functioning at full efficiency. Dirty or hot intake air; carbon accumulations in the valves, cylinders, or lines; dirty water jackets and intercooler tubes; improper lubricants; and leaky lines are particularly important, since they not only reduce efficiency but also cause costly shutdowns for repairs. These points are discussed in detail. E.J.V.

Diesel performance. W. F. SCHAPHORST. *Refiner & Natural Gasoline Mfr.*, **16** [3] 146 (1937).—Rough calculations for determining the amount of fuel consumed and the efficiency of any size Diesel engine are given. Curves

showing pounds of fuel per horse power per hour for engines up to 3000 h.p. with examples of calculations are presented. For small engines of 50 h.p. or less the fuel consumption is 0.45 lb./ h.p., while for engines of 1000 to 3000 h.p. the figure is 0.39 lb./h.p. The efficiency of any size engine with any fuel may be calculated by multiplying the B.t.u. value of the fuel per pound by the number of pounds per horse power per hour and dividing the product into 2546. J.J.H.

Driers for roofing tile. T. A. Goskar. *Brit. Clayworker*, **46** [549] 366–70 (1938).—A general discussion of artificial driers and their advantages over other methods of drying is given. R.A.H.

Drying of solid bodies: XVI–XXV. S. Kamei and S. Shiomi. *Jour. Soc. Chem. Ind. Japan*, **40** [7] 251–63B; [8] 325–37B; [10] 366–77B (1937); for Part **XV** see *Ceram. Abs.*, **15** [3] 100 (1936). M.V.C.

Electric shaker conveyers. Anon. *Indian & Eastern Engr.*, **80** [2] 196–98 (1937).—The "Meco" electric shaker conveyer driving gear of modern design and construction, manufactured by the Mining Engineering Co., Ltd., of Worcester, England, is described with illustrations. A.P.S.

Elements of automatic control. John J. Grebe. *Ind. Eng. Chem.*, **29** [11] 1225–28 (1937).—Common experience is used to illustrate the problems met in connection with automatic control and the principles of operation used. Four basic elements of control are derived: metered, deviation, rate, and damping control; they are illustrated by various kinds of automatic control equipment. G. gives a direct measure for control performance by determining the time required to reëstablish equilibrium in terms of the total transfer time lag. Illustrated. F.G.H.

Evaluation of sedimentation tests. P. Debye. *Rev. Universelle Mines*, **11** [8] 266–68 (1935).—D. describes a method for determining the composition of powders, *i.e.*, the size of the particles they contain, by means of dielectric measurements. E.W.S.

Filter polarizers and their field of use. M. Haase. *Glastech. Ber.*, **15** [8] 295–99 (1937). J.F.H.

Flotation of nonsulfidic minerals. J. Kraft Johanssen. *Tids. Kjemi Bergvesen*, **17**, 101–108 (1937); abstracted in *Chem. Zentr.*, **1937**, ii, 4220.—J. gives a comprehensive review of flotation methods for obtaining quartz, witherite, ilmenite, kyanite, carnotite, etc. Na silicate, used as water glass, plays an important rôle as flotation reagent in this method. M.V.C.

Grinding, mixing, and clay preparation in the clay industry. W. Neimann. *Tonind.-Ztg.*, **61** [57] 631–33; [59] 654–58 (1937). **In the brick, roof tile, and stone ware industry.** *Ibid.*, [58] 646–49.—N. gives a general review of the more common methods and machines used in the preparation of the body in the heavy clay industry. W.K.

Materials for sleeve joints of pipes. E. Landel. *Gas- & Wasserfach*, **80** [32] 572–74 (1937).—In comparison with other jointing materials (jute, wood wool, paper, cellulose, hemp), Al foil has given perfectly satisfactory and dense joints in sleeves up to 300 mm. diameter according to observations in the water system of the city of Stuttgart. M.H.

Mechanical handling at clay pits. Mavor and Coulson, Ltd. *Mech. Handling*, **24**, 153–55 (1937).—An installation of two belt conveyers, made from units 12 ft. long, for taking clay from a multibucket excavator to the mixers at Herfield Bricks, Ltd., Sussex, England, is briefly described and illustrated. J.C.C.

Metallurgical progress and the clayworking industry. Anon. *Brit. Clayworker*, **46** [550] 396–98 (1938).—Improvements in metals for machinery used in the clayworking industry are reviewed. See *Ceram. Abs.*, **16** [5] 157 (1937). R.A.H.

Method for photographing petrographic thin sections at low magnifications. Wilton J. Crook. *Amer. Mineralogist*, **23** [2] 114–16 (1938).—C. places the thin section in an enlarger and focuses the image on a plate or film from which contacts can be made later. F.J.Z.

Ore concentration process. E. Bierbrauer. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 204–208 (1937).—B. has developed a new method for dressing and separating coarse-grained mineral mixtures, which applies the principle of boundary faces used in the flotation process. If ice is used as the adhesive substance, hydrophobic grains do not freeze to it but hydrophilous grains do. If a hydrophobic organic adhesive substance is employed, the process of adhesion is reversed. The method is called the "picking process." A coarse-grained mixture of phosphorite and quartz of 20 to 60 mm. was separated by this process by treating it with a 1% aqueous solution of sodium palmitate, to which preferably 2% petroleum or another oil is added. This mixture is placed on the adhesive mass, *e.g.*, a bitumen (naphtha) solid, at normal temperature. After 1 to 2 min. the phosphorite grains stick to the mass, while the quartz grains do not and drop off upon rotation of the support. If ice is used, the quartz grains stick, and the phosphorite drops off. For grain sizes from 5 to 15 mm. the concentration of phosphorite was 89.6%, and for sizes from 15 to 30 mm., 98%. Experiments with magnesite-serpentine, calcite-quartz, bitumen containing slate, etc., gave similar results. Practical arrangements for continuous application are described. M.H.

Practical experiences in the de-airing of heavy clay goods. A report on a questionnaire. F. H. Clews. *Brit. Clayworker*, **46** [549] 371–73 (1938).—C. reports on a questionnaire sent to English firms for information on results of de-airing practices similar to a questionnaire sent to manufacturers in the U. S. (*Bull. Amer. Ceram. Soc.*, **15** [10] 335–40 (1936)). R.A.H.

Self-filling pycnometer. G. F. Hennion. *Ind. Eng. Chem., Anal. Ed.*, **9** [10] 479 (1937).—Details of construction are given. Illustrated. F.G.H.

Small set of grids for the determination of nonopaque minerals. J. D. H. Donnay. *Amer. Mineralogist*, **23** [2] 91–100 (1938). F.J.Z.

Thermal conductivity at elevated temperatures. W. George Johnson. *Refiner & Natural Gasoline Mfr.*, **16** [4] 173 (1937).—J. deals especially with the relative thermal conductivities of a semicorrosion-resisting, high strength, chrome steel and corrosion-resisting, scale-resisting, high-strength, chrome irons, chrome-nickel steels, and chrome-nickel-silicon steels, as compared with plain carbon steel at elevated temperatures. He cites the work of Edward Maurer with results of tests obtained on 13 types of irons and steels at temperatures ranging from 30°

to 1200°C. The type of apparatus used and the testing procedure are explained. J. finds that, for fairly low temperatures, plain carbon steel is somewhat superior in thermal conductivity to low chrome steels, chrome irons, chrome-nickel steels, and chrome-nickel-silicon steels. As the temperature is increased, points are reached for certain grades where the superiority is reversed, *i.e.*, the plain carbon steels are inferior. J.J.H.

Ultracentrifuge of high efficiency. H. KAUNITZ AND A. MARKO. *Mikrochim. Acta*, **2**, 24–33 (1937); *Chem. Abs.*, **32**, 393 (1938).—An ultracentrifuge which is suitable for work with 1.6 ml. of liquid and can be driven at 200,000 r.p.m. is described. The middle part of the liquid is subjected to a centrifugal force equal to 465,000 times the force of gravity. The apparatus is driven by compressed air and, for the sake of safety, is encased in steel. It is provided with a photoelectric speed counter, an automatic regulator for controlling the influx of compressed air, and a device for withdrawing liquid by suction from any desired level, even when the machine is operated at its highest speed.

Use of the microscope. H. WRIGHTON. *Iron & Coal Trades Rev.*, **135** [3644] 1080 (1937).—W. discusses the selection of proper instruments, preparation of specimens, and the best technique in application to obtain maximum efficiency in industrial research. M.H.

Viscosmeter for viscosity determination of fused glasses and slags. K. S. EVSTROP'EV AND A. S. GORALNIK. *Zavodskaya Lab.*, **6**, 591–94 (1937).—The construction and operation of a modified Frank viscometer are illustrated and described. See "Viscosity—," *Ceram. Abs.*, **15** [10] 299 (1936). P.B. & E.S.

REPORTS

Active list of permissible explosives and blasting devices approved prior to June 30, 1937. ANON. *U. S. Bur. Mines Repts. Investigations*, No. 3361, 22 pp. Free. The report lists 196 brand names. R.A.H.

Bureau of Mines midget impinger for dust sampling. J. B. LITTLEFIELD, FLORENCE L. FEICHT, AND H. H. SCHRENK. *U. S. Bur. Mines Repts. Investigations*, No. 3360, 4 pp. Free. A small, portable, hand-operated impinger is described. Results obtained with this machine agree well with those obtained with regular impingers. R.A.H.

PATENTS

Apparatus for cleaning articles of ceramic materials. H. V. SCHWEITZER. Brit. 480,168, March 2, 1938 (Nov. 11, 1935).

Apparatus for marking or decorating articles. DAVID DENELSBECK (Owens-Illinois Glass Co.). U. S. 2,111,207, March 15, 1938 (Dec. 30, 1933).

Apparatus and method for making mineral wool. H. F. VIEWEG (Johns-Manville Corp.). U. S. 2,110,280, March 8, 1938 (May 13, 1936).

Briquetting machine. R. W. DINZL (Baldwin-Southwark Corp.). U. S. 2,110,972, March 15, 1938 (March 18, 1937).

Ceramic article making apparatus. A. H. FESSLER AND RALSTON RUSSELL, JR. (General Motors Corp.). Can. 371,806, Feb. 8, 1938 (June 15, 1936); see *Ceram. Abs.*, **16** [11] 346 (1937). G.M.H.

Cyclone apparatus for separating solid particles from gases. T. C. BIETH. Can. 371,363, Jan. 18, 1938 (Dec. 14, 1935). G.M.H.

De-airing and degassing ceramic bodies. GEWERKSCHAFT KERAMCHEMIE-BERGGARTEN. Brit. 479,157, Feb. 16, 1938 (Dec. 7, 1935).

Drying plant for pottery, etc. MAX KOTTERBA. Ger. 651,838, Oct. 20, 1937; Cl. 82*a*. 2; *Chem. Abs.*, **32**, 744 (1938).

Dust extracting method. R. F. KNEISLEY (American Floor Surfacing Machine Co.). Can. 371,114, Jan. 11, 1938 (Dec. 10, 1936). G.M.H.

Fluid pressure regulator. G. K. O'CONNOR (Smoot Engineering Corp.). Can. 371,164, Jan. 11, 1938 (July 10, 1936; in U. S., July 15, 1935). G.M.H.

Furnace and method of firing. W. S. MCVAY (E. I. du Pont de Nemours & Co.). U. S. 2,108,292, Feb. 15, 1938 (April 21, 1936). A furnace comprises a combustion chamber situated on a higher plane than the lower portion of the object being heated and horizontally opposite a higher portion of the object, a chamber enclosing the object and connecting indirectly at the top through and around a baffle wall with the combustion chamber and at the bottom with a flue, the baffle wall being situated horizontally between the combustion chamber and the object being heated and being adapted to prevent direct impingement of flame and gases from the combustion chamber upon the object.

High-temperature controlling method. H. K. RICHARDSON AND F. A. NEWCOMBE (Canadian Westinghouse Co., Ltd.). Can. 371,460, Jan. 25, 1938 (Dec. 13, 1935). G.M.H.

Machine for printing directly on metal or glass, etc. FREDERICK SHURLEY (Ceramic Machinery Distributors, Ltd.). U. S. 2,108,597, Feb. 15, 1938 (Feb. 14, 1934; Dec. 30, 1935).

Means for casting clay pipe. WILLIAM WASHO (Pacific Clay Products). U. S. 2,109,078, Feb. 22, 1938 (Dec. 4, 1935). In a device for casting clay pipe, a lower tubular mold formed integral having a lower internal shoulder sloping inwardly and downwardly and a lower outward flare below the shoulder to the bottom of the lower portion of the mold, an upper mold section having a transverse joint with the lower mold connected by interfitting recesses and dowels, the upper mold having a plurality of vertical joints with interconnecting recesses and dowels, the upper mold having a collar forming enlargement with a lower shoulder sloping outwardly and upwardly, an annular surface thereabove having an outward slope, an upper shoulder sloping upwardly and inwardly and having a funnel surface sloping upwardly and outwardly from the inner edge of the second shoulder, the upper and lower molds being relatively thick compared to their internal diameter and formed of a water-absorbent material, the upper funnel surface being adapted to operate as a guide for a clay trimming tool at the top of the mold, and the lower flared surface being adapted to act as a guide for a trimming tool at the lower part of the mold.

Process and installation for making pottery. W. J. MILLER. U. S. 2,109,028, Feb. 22, 1938 (Nov. 4, 1931).

Sedimentation device. W. E. MESSER (Dorr Co., Inc.). Can. 371,799, Feb. 8, 1938 (Nov. 29, 1935; in U. S., Dec. 22, 1934). G.M.H.

Tile-fettling mechanism. E. B. COLLINGHAM AND C. J. A. OWEN. Brit. 479,604, Feb. 23, 1938 (Aug. 11, 1936).

Kilns, Furnaces, Fuels, and Combustion

Coal hydrogenation. Primary liquefaction by destructive hydrogenation of the oxygen, nitrogen, and sulfur linkages. C. H. FISHER AND ABNER EISNER. *Ind. Eng. Chem.*, **29** [12] 1371–76 (1937).—To obtain information regarding the elimination of the inorganic elements in the coal substance during the primary liquefaction, a Pittsburgh bed coal was hydrogenated in tetrahydronaphthalene for 3, 6, 9, and 12 hr. at 385°, 400°, and 415°C. The most marked changes occurred in the first 3-hr. period when about 60% of the oxygen was removed. The remaining 40% of the oxygen was eliminated with much greater difficulty. These results appear to indicate that at least two types of oxygen linkage are present in coal. The elimination of nitrogen was very slow and approximately constant. Sulfur removal, which occurred to the greatest extent in the first 3 hr., was also slow. Several conclusions, which must be regarded as tentative until confirmed by later work, were drawn from the analytical and yield data concerning the mechanism of the primary liquefaction and the nature of the oxygen linkages in coal. Illustrated. See *Ceram. Abs.*, **17** [1] 34 (1938). F.G.H.

Coal hydrogenation. U. S. Bureau of Mines experimental plant. H. H. STORCH, L. L. HIRST, P. L. GOLDEN, I. I. PINKEL, R. L. BOYER, J. R. SCHAEFFER, AND R. H. KALLENBERGER. *Ind. Eng. Chem.*, **29** [12] 1377–80 (1937).—An experimental plant for the continuous hydrogenation of about 100 lb. of coal/24 hr. is described. The major difficulties experienced in the operation of the plant and the solutions adopted are discussed. Typical results on the liquid-phase hydrogenation of Pittsburgh seam coal are given. Illustrated. F.G.H.

Design and firing of kilns: I, Study and record of modern practice. ANON. *Brit. Clayworker*, **46** [550] 385–88 (1938).—The design, setting, and firing of a Scotch kiln, the downdraft kiln in general, and the beehive type in particular are discussed. R.A.H.

Dust removal from chimney gases. D. BROWNLIE. *Steam Engr.*, **7**, 137–39 (1938).—The removal of dust from the chimney gases of the Boston Edison Co. by water-scrubbing is described. L.R.B.

Effect of thermal insulation of arc furnaces on current consumption. H. WEITZER. *Stahl & Eisen*, **57**, 697–702 (1937).—The characteristics of six Austrian furnaces were investigated, especially the relations between current consumption, melting time, and furnace life. Attempts to reduce the radiation loss by thickening the walls and the roof and so reducing the temperature of the cold face are useless, since the heat loss is only shifted. Losses in heating up and shutdowns are reduced by choosing a constructional material of low thermal conductivity. Insulation with Thermalite and two types of diatomite brick showed reductions in melting current of 3 to 6% and in melting time, of 11%. The replacement of 380 of the cooler magnesite brick by the (cheaper) diatomite brick resulted in a saving of 475 Austrian schillings per lining. A discussion is included. L.R.B.

Electric furnaces in ceramics. M. D. *Argile*, No. 1, pp. 9–15 (1938).—Electric furnaces of the resistance type for firing ceramic products are briefly discussed. The advantages of electric furnaces are noted. M.V.C.

Electric heat in industry. H. MASUKOWITZ. *Eng. Progress*, **18** [12] 261–66 (1937).—M. briefly reviews the uses of electric heat in various industries. In ceramics, he cites the firing of stoneware, terra cotta, tile, etc., in electric tunnel kilns. The firing of colors on glass and ceramic ware is increasingly carried out in electric furnaces. Leers in the glass industry are being fired electrically, and the vitreous enamel industry is using more electric furnaces. 21 photographs. See "Application—" *Ceram. Abs.*, **17** [3] 112 (1938). J.L.G.

Industrial propane as a glass-plant fuel. ANON. *Glass Ind.*, **18** [11] 377–80 (1937).—Propane is a hydrocarbon which, although normally gaseous, may be liquefied at ordinary temperatures and moderate pressures. It can be vaporized under ordinary conditions without the application of heat, and because of its high vapor pressure it accomplishes certain savings through the use of higher distribution pressures. Combustion systems and burners used for burning industrial propane include nozzle mixing, atmospheric low-pressure premix, and high-pressure premix burners. In addition to its use as a primary fuel, propane is being used in some large plants to enrich other low heating value gases, such as coke-oven or blast-furnace gas, providing a satisfactory fuel for luminous-flame installations. The burner systems are discussed in detail, together with examples of industrial applications. E.J.V.

Natural gas in Europe. LEGRAYE. *Rev. Universelle Mines*, **11** [7] 232–35 (1935).—Sources of natural gas are described, the most important being in Poland, Rumania, and the U.S.S.R., with figures on its utilization. The author finds that a considerable amount of such gas is wasted, that the production of by-products (gasoline and carbon black) is often imperfect, and that the industrial and domestic uses of the gas have been little developed. Some of these sources of natural gas, but not all, are close to deposits of petroleum. E.W.S.

Phase equilibria in hydrocarbon systems: XIX, Thermodynamic properties of *n*-butane. B. H. SAGE, D. C. WEBSTER, AND W. N. LACEY. *Ind. Eng. Chem.*, **29** [10] 1188–94 (1937).—Specific volumes and latent heats of vaporization of *n*-butane were experimentally determined at temperatures from 70° to 250°F. From these and other published data the changes in enthalpy, entropy, and fugacity with temperature and pressure were calculated. The results are presented in tabular and graphical form. **XX, Isobaric heat capacity of gaseous propane, *n*-butane, isobutane, and *n*-pentane.** *Ibid.*, [11] 1309–14.—Isobaric heat capacities at atmospheric pressure were determined for gaseous propane, *n*-butane, isobutane, and *n*-pentane at temperatures from 90° to 320°F. Several diagrams show the agreement of these measurements with the data

of other investigators. Illustrated. For Part **XVIII** see *Ceram. Abs.*, **16** [8] 254 (1937). F.G.H.

Smoke emission in the clay industry, particularly in the heavy clay industries. E. ROWDEN AND A. T. GREEN. *Proc. Nat. Smoke Abatement Soc., 8th Ann. Conference, Oct., 1936*, pp. 31–51; *Chem. Abs.*, **31**, 8062 (1937).—A discussion is given.

Sulfur removal from combustion gases. D. BROWNLIE. *Steam Engr.*, **6**, 508–10 (1937).—B. describes the results obtained by H. F. Johnstone at the Univ. of Illinois in the elimination of sulfur dioxide from waste combustion gases. See *Ceram. Abs.*, **17** [3] 113 (1938). L.R.B.

Thermodynamics in hydrocarbon research. CHARLES L. THOMAS, GUSTAV EGLOFF, AND J. C. MORRELL. *Ind. Eng. Chem.*, **29** [11] 1260–67 (1937).—The differences between thermodynamic data from calorimetric measurements and those calculated from Raman and infra-red spectra are discussed. The new equation, $\Delta F°_T = -10{,}550 - 5890n + 25.2nT - 2.2T(n>1)$, has been derived for straight-chain paraffin hydrocarbons. Similarly, the new equation, $\Delta F°_T = 20{,}321 - 5835n - 33.26T + 24.52nT$ $(n>2)$, has been derived for straight-chain olefins with the double bond in the terminal position. A table of standard free-energy values for 42 hydrocarbons at 298°, 500°, and in some cases at 1000°K is given. These data may be used to decide whether a reaction is thermodynamically possible and what temperature is advisable for finding a catalyst for the reaction. F.G.H.

Why so many kinds of electric resistance furnaces? G. SIMON. *Elektrowärme*, **8** [1] 11–20 (1938).—S. gives an exhaustive survey with diagrammatic representation of 30 types and the fields for which their application is indicated. M.H.

Zig-Zag kiln. A complete technical analysis. V. BODIN. *Brit. Clayworker*, **46** [549] 355–57 (1938). R.A.H.

PATENT

Tunnel furnace for ceramic products. SOC. DES FOURS INDUSTRIELS ET MÉTALLURGIQUES. Fr. 811,785, April 22, 1937; *Chem. Abs.*, **32**, 744 (1938).

Geology

Bentonite. VICTOR CHARRIN. *Rev. Matériaux Construction Trav. Publics*, No. 336, pp. 129–30B (1937).—The characteristics and uses of bentonite from Wyoming are briefly discussed. See *Ceram. Abs.*, **16** [5] 159 (1937). M.V.C.

Bibliography on properties and uses of bentonite. G. R. WOODWARD. *Bull. Brit. Cast Iron Research Assn.*, **4** [4] 465–66 (1937).—The bibliography contains 25 references and covers the period 1920 to 1936. A.P.S.

Classification of the natural silicates: I. CHARLES K. SWARTZ. *Amer. Mineralogist*, **22** [11] 1073–87 (1937).—The fundamental fact in the classification of the silicates is the combination of SiO_4 tetrahedra by their solid angles. Five fundamental types are developed upon this basis and described. S. shows that the fundamental types may combine further to form complex types, whose characteristics are considered. The relation of this classification to earlier classifications is discussed. **II.** *Ibid.*, [12] 1161–73.—The compositions and classification of the species of natural silicates are given as far as they have been determined by X-ray investigation, with references to the literature in which their structure is described. F.J.Z.

Contemporaneous crystallization of beryl and albite *versus* replacement. B. M. SHAUB. *Amer. Mineralogist*, **22** [10] 1045–51 (1937).—The beryl-albite intergrowths occurring at the Golding-Keene and the Strichland feldspar mines are of such a nature that an origin through the process of replacement is most unlikely; their relationship and other features clearly indicate a contemporaneous crystallization. F.J.Z.

Deformation of single calcite crystals under high confining pressures. DAVID GRIGGS. *Amer. Mineralogist*, **23** [1] 28–33 (1938).—To supplement the work of investigation of the characteristics of deformation of the calcite aggregates, limestone and marble, some experiments of the deformation of single crystals of calcite under conditions of high confining pressures were performed. The change in properties with pressure is remarkably different from changes observed in the aggregates, which suggests the possibility that a considerable portion of the deformation of the aggregates takes place by intercrystalline deformation. The mechanism of deformation of single crystals does not change with pressure alone, and $10\bar{1}2$ twinning is the dominant means of deformation. G. finds that twinning occurs on those twin planes where the deforming force resolved on the plane and in the direction and sense of twinning is maximum. F.J.Z.

Deposits of crystalline magnesite and their distribution in the mountain structure of the eastern Alps. R. SCHWINNER. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 306–14 (1937).—S. gives an exhaustive description of the origin, formation, and geological, stratigraphical, and geographical conditions, illustrated by charts showing details of the magnesite and talc deposits. M.H.

Development of mechanical analysis of soil. VÁCLAV NOVÁK. *Trans. Internat. Congr. Soil Sci., 3d Congress, Oxford, 1935*, **2**, 23–36 (1935); *Chem. Abs.*, **32**, 702 (1938).—A brief historical review is given.

Geology and mining of the chrome-iron ore deposits of the Balkan mountains. G. HEISSLEITNER. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 338–44 (1937).—The peridotite serpentine ores form the bulk of the deposits and contain 40 to 48% Cr_2O_3; the production amounts to 8% of the world production. The ores with 40% Cr_2O_3 are almost exclusively used in the refractories industry, and the richer ores are used for the production of ferrochromium, 60 to 70% Cr, and for high-grade refractories. Geological conditions, geographical distribution, and mining methods are discussed. M.H.

Heavy minerals in granitic rocks of the Yosemite region. ADOLPH PABST. *Amer. Mineralogist*, **23** [1] 46–53 (1938). F.J.Z.

Lapis lazuli from San Bernardino County, California. AUSTIN F. ROGERS. *Amer. Mineralogist*, **23** [2] 111–14 (1938).—A description of the rock from its only known locality in North America is presented. F.J.Z.

Leightonite, a new sulfate of copper from Chile.

CHARLES PALACHE. *Amer. Mineralogist*, **23** [1] 34–37 (1938).—Leightonite, $CuO{\cdot}2CaO{\cdot}K_2O{\cdot}4SO_3{\cdot}2H_2O$, a new copper mineral from Chuquicamata, Chile, is described, and its optical properties are presented. F.J.Z.

Mineral production of India during 1936. A. M. HERON. *Records Geol. Survey India*, **72** [3] 237–332 (1937).—Data are presented on chromite, coal, copper, ilmenite, iron, magnesite, manganese, petroleum, and refractory minerals. A.P.S.

Observations on bauxite. V. CHARRIN. *Argile*, No. 1, pp. 1–5 (1938).—The opinion that bauxite is a variety of clay is misleading. The characteristics of both materials are discussed in detail, and French bauxite deposits are analyzed. See *Ceram. Abs.*, **16** [3] 97, 99 (1937). M.V.C.

Occurrence of gypsum in Kentucky. A. C. MUNYAN. *Amer. Mineralogist*, **22** [10] 1069–72 (1937). F.J.Z.

Ore district of Panagjurischte in Bulgaria. K. A. GEORGIEFF. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 320–30 (1937).—Topography, petrography, and geological conditions are described in detail. Metamorphous, magmatic, and sedimentary rocks are present, including andesite, slates, marl ($CaCO_3$), and ore bearing veins of Cu, Fe, and S, with traces of Zn, As, and Au, and containing 12 g. Ag/ton. M.H.

Ore range of Karamazar in western Turkestan. H. WELSER. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 392–97 (1937).—W. describes briefly the geographical distribution of deposits of Pb, Zn, Ag, Au, As, Cu, W, and U with Ra. M.H.

Organic matter in Arkansas bauxite. Origin and nature. DON UTLEY. *Ind. Eng. Chem.*, **30** [1] 35–39 (1938).—The bulk of the organic matter in Ark. bauxite comes from the overburden, especially from the lignitic clays. It is composed mostly of humic acids, humates, and their oxidation products. The oxidation products of these humic acids, after extraction with sodium hydroxide, may be separated into fractions insoluble in mineral acids but soluble in ethyl alcohol, soluble in acids but precipitated with aluminum hydroxide in neutral solution, and soluble in neutral solution. Analyses of the fractions separated are given where isolation was possible. Tests for specific compounds usually occurring in soils were negative. Fairly pure samples of humic acids were obtained from the lignites and analyzed. Analyses of inorganic material combined with humic acids from lignite and bauxite are given, and the chemical difference is shown. A satisfactory method for the determination of organic matter in bauxite is presented. Illustrated. F.G.H.

Origin and coloring of clays. GEORGES VIE. *Argile*, No. 1, pp. 21–23 (1938).—Clay, a hydrated silicate of aluminum, has a badly defined origin. Assumptions dealing with the formation of clays, such as thermal influences and weathering, are briefly discussed. The red coloring of clay, attributed to iron salts, is considerably accentuated by the presence of titanium. The coloring of French clays is discussed. M.V.C.

Origin of montmorillonite. W. HAROLD TOMLINSON AND ADOLPH E. MEIER. *Amer. Mineralogist*, **22** [11] 1124–26 (1937).—The reaction of formation of a clay mineral at Glenn Riddle, Delaware County, Pa., is expressed as follows: plagioclase + basic magnesium carbonate + water = montmorillonite + calcium carbonate + sodium carbonate. The last two salts are removed in solution. F.J.Z.

Particle size in relation to base exchange and hydration properties of Putnam clay. D. M. WHITT AND L. D. BAVER. *Jour. Amer. Soc. Agron.*, **29**, 905–16 (1937); *Chem. Abs.*, **32**, 701 (1938).—Particles of the size used in this investigation are stable under rather drastic dispersion treatments. The 2-micron fraction was resuspended 211 times. Particles below 1 micron possess very different properties from the particles above this size. The fraction between 1 and 0.5 micron is almost entirely absent in this soil, but its properties can be obtained by interpolation. The property of swelling is not present in particles greater than 1 micron, and the maximum toluene adsorption takes place in the same particle-size range. A sharp break in exchange capacity also occurs near this point. On the basis of these few properties, 1 micron is not far from the upper limit of colloidal size in Putnam silt loam.

Philippine chromite. ANON. *Mineral Ind.*, **45**, 61 (1936).—Beginning in 1937, 28,000 tons of ore from the Masinloc deposit were to be shipped to the U. S. A chromite deposit also occurs at Zimbales. B.C.R.

Present-day scientific knowledge in the service of the ceramic industry. MAURICE DÉRIBÉRÉ. *Argile*, No. 169, pp. 5–9; No. 170, pp. 17–21 (1937); see *Ceram. Abs.*, **16** [3] 98 (1937). M.V.C.

Productive feldspar and kaolin deposits in middle, east, and south Europe and their economical importance. F. KIRNBAUER. *Berg- & Hüttenmänn. Jahrbuch Montan. Hochschule Leoben*, **85** [3–4] 291–97 (1937).—Geological and geographical conditions are described, and statistics on production and exports are given. Czechoslovakia produces between 300,000 and 400,000 tons of kaolin per year. M.H.

Properties of Indian bentonites. D. R. MITRA AND A. REID. *Proc. Indian Sci. Congr., 25th Congr.*, **1938**, Part 3, p. 99.—The chemical and physical properties of seven Indian bentonites are discussed and contrasted with those of a treated American bentonite. Of the seven, four are believed to be true bentonites; the others are sub-bentonites. Three are mixtures of alkali and alkali-earth bentonites, while the American is a true alkali bentonite. The fourth is a calcium bentonite readily converted to the sodium form by base exchange. The Indian samples give stable suspensions at low concentrations with the exception of the calcium bentonite, which on base exchange gives very stable suspensions. Hydrogen-ion concentration values of these suspensions vary with time but eventually become constant. Six of the samples pass the suggested MgO test for bentonite; the calcium bentonite easily passes after base-exchange treatment. Thixotropy is developed to a varying extent by suspensions of the bentonite in water, that of the calcium bentonite being greatly enhanced on conversion to the sodium form. The samples show varying degrees of efficiency in increasing the viscosity of drilling fluids, none of them approaching in effectiveness the American product. The Indian bentonites can possibly be improved by suitable treatment; a few commercial uses are suggested. A.P.S.

Properties and uses of lithium. J. STAES. *Rev. Universelle Mines*, **10**, 635–37 (1934).—S. gives an exhaustive

description of the physical and chemical properties of lithium, occurrence of its ores, uses of lithium-containing rocks in glass and porcelain making, uses of lithium and lithium salts, liberation of the metal, and its use in alloys. E.W.S.

Pyrophyllite talc mining booms in North Carolina. ANON. *Eng. Mining Jour.*, **139** [1] 36–37 (1938).—Pyrophyllite is a hydrous aluminum silicate physically quite similar to steatite, hydrous magnesium silicate. Pyrophyllite mining has recently expanded in N. C., until there are now six grinding plants working on this mineral. The plant of Pyrophyllite Talc Products, Inc., at Glendon, is described. Accessory minerals are quartz, sericite, graphite, occasional cubes of pyrite, chloritoid, and traces of limonite. The pyrophyllite often grades imperceptibly into sericite. Recent ceramic researches indicate that it can be used to replace Cornwall stone in wall-tile bodies. It gives great uniformity over the firing range and lowers moisture expansion. In white tile it prevents crazing. It is also used in talc-porcelain bodies. Vitrified talc-porcelain bodies are tough but have a relatively short firing range. Pyrophyllite is said to be useful in making fire brick, refractory cements, and plastics. Analyses by J. L. Stuckey are as follows: pyrophyllite: water (loss on ignition) 5.54, silica 64.68, alumina 28.34, ferrous oxide 0.60, magnesia trace, soda 0.38, and potash 0.01%; sericite: water (loss on ignition) 5.05, silica 47.07, alumina 36.89, ferrous oxide 0.42, magnesia 0.20, soda 1.34, and potash 8.21%. Two photographs. J.L.G.

Rare alkali biotite from Kings Mountain, North Carolina. FRANK L. HESS AND ROLLIN E. STEVENS. *Amer. Mineralogist*, **22** [10] 1040–44 (1937). F.J.Z.

Recent data on bentonite of Tétény. M. VENDL. *Magyar Kir. József Nádor Műszaki és Gazdaságtudományi Egyetem Bánya-, Kohó- és Erdőmérnöki Kar, Sopron. A bánya és kohómérnöki osztály Közleményei*, **9**, 320–26 (1937). —New results of investigations on the nature of bentonite show that it is a clayey ash tuff embedded in the Sarmatian limestone and must be considered as montmorillonite of an andesitic type, the vitreous basis of which has been devitrified. 20 references. M.H.

Recent developments in the use of contact clays. S. R. FUNSTEN. *Refiner & Natural Gasoline Mfr.*, **16** [6] 237 (1937).—F. discusses (1) laboratory and plant test data on various clays, (2) a test method of determining the decolorizing efficiencies of contact clays, and (3) plant clay handling and mixing equipment. Numerous charts of physical, chemical, and cost data are included. J.J.H.

Refractory clays of the Belkinskiĭ deposits. D. P. ZEGZHDA. *Ogneupory*, **4** [5] 307–11 (1936).—The large deposits of plastic Belkinskiĭ clays are described. The chemical, mechanical, ceramic, and physicochemical properties of these clays are discussed. M.V.C.

Relation of leightonite to polyhalite. M. A. PEACOCK. *Amer. Mineralogist*, **23** [1] 38–45 (1938). F.J.Z.

Riebeckite in quartz veins from the Michipicoten district, Ontario. J. E. HAWLEY. *Amer. Mineralogist*, **22** [11] 1099–1103 (1937).—A fibrous variety of riebeckite is described as occurring in quartz veins and in both granitic and basic volcanic wall rocks in the Michipicoten area, Ontario. It represents one of the last stages of hydrothermal alteration, replacing all other minerals present, particularly quartz, greenish muscovite, epidote, and carbonates. F.J.Z.

Scientific manufacture of ceramic building materials. F. CHALAMEL. *Rev. Matériaux Construction Trav. Publics*, No. 329, pp. 21–23B; No. 330, pp. 38–40B; No. 331, pp. 52–58B; No. 331, pp. 68–76B; No. 333, pp. 82–88B (1937).—C. gives a detailed analysis of the composition of French raw materials, in particular feldspar, used in the manufacture of stoneware tile; the manufacturing procedure is described. See *Ceram. Abs.*, **16** [6] 179 (1937). M.V.C.

Selective incrustation of minerals. CLIFFORD FRONDEL. *Amer. Mineralogist*, **22** [11] 1104–16 (1937).—The crystallization of one mineral upon another in the formation of a a mineral incrustation is, in general, influenced by adsorption at the boundary between the incrusted crystal and the solution. When a mineral crystallizes in the presence of drusy crystals of several earlier-formed species, adsorption may induce the selective incrustation of one of the species. Chemical reaction between a solution or sol and the surface of the incrusted crystal (chemosorption) may also affect selectivity. Instances of incrustations selective between minerals are described, and the incrusting relations of several groups of common minerals are discussed in the light of such evidence and experimental adsorption data. Minerals which are identical or nearly identical in crystal structure have a marked tendency to incrust each other in preference to other species. Quartz and the members of the calcite group have a tendency toward crystallization upon each other. Quartz and the metallic sulfides either are without a tendency for crystallization upon each other or, more probably, are antipathic in this relation. The metallic sulfides tend to crystallize upon the minerals of the calcite group and upon fluorite. F.J.Z.

Structural investigation of the isomorphism of the apatite group. DUNCAN MCCONNELL. *Amer. Mineralogist*, **23** [1] 1–19 (1938).—All of the minerals examined are structurally similar to apatite, *i.e.*, they have the space group C^3_{6h}, as indicated by the similarities of the spacings and the intensities of their powder diagrams. The formulas, lattice dimensions, and densities of representative specimens are given in tabular form. The isomorphism of this group is considerably more complicated than has been previously recognized. The value of accurate and complete analyses can not be overemphasized in connection with any further investigations of these minerals. Analyses which are incomplete or which were made by methods now obsolete or on heterogeneous materials are almost valueless for this work in view of the complexity of the isomorphism. F.J.Z.

Structural relationships of kaolinites and anauxites. F. MACHATSCHKI. *Amer. Mineralogist*, **23** [2] 117–18 (1938). F.J.Z.

Taenolite from Magnet Cove, Arkansas. H. D. MISER AND R. E. STEVENS. *Amer. Mineralogist*, **23** [2] 104–10 (1938).—The physical and optical properties, chemical analysis, and X-ray pattern of taenolite, an exceedingly rare lithium-magnesium mica, are given. F.J.Z.

BOOK AND BULLETIN

Bibliography of North American Geology for 1935 and

1936. E. M. THOM. *U. S. Geol. Survey Bull.*, No. 892, 504 pp. Supt. of Documents, Govt. Printing Office, Washington, D. C. Price 50¢. The bibliography of North American geology, including paleontology, petrology, and mineralogy, lists publications on the geology of the continent of North America, adjacent islands, Panama, and the Hawaiian Islands. It includes textbooks and papers of general character by American authors but not those by foreign authors, except papers that appear in American publications. See *Ceram. Abs.*, **15** [7] 218 (1936).

R.A.H.

Industrial Minerals and Rocks (Nonmetallics Other than Fuels). Edited by SAMUEL H. DOLBEAR, Chairman, AND OLIVER BOWLES, Vice-Chairman, Committee on the Industrial Minerals Volume. American Institute of Mining and Metallurgical Engineers, New York, 1937. 955 pages. Price $6 net. Briefly reviewed in *Eng. Mining Jour.*, **139** [1] 58 (1938).—This compact library on the nonmetallics consists of 48 chapters, each written by a specialist on the mineral or group of minerals treated.

J.L.G.

PATENTS

Magnesium production. DANIEL GARDNER. Can. 371,550 to 371,555, Jan. 25, 1938 (Dec. 3, 1936).

G.M.H.

Mineral separator. W. H. BERRISFORD. Can. 371,751, Feb. 8, 1938 (June 16, 1934). G.M.H.

Chemistry and Physics

Atomic packing models of some common silicate structures. J. E. DORRIS, CLIFFORD FRONDEL, W. C. GÖSSOW, V. M. LOPEZ, C. S. LORD, WILLIAM PARRISH, AND J. A. SHIMER. *Amer. Mineralogist*, **23** [2] 65–84 (1938).—Construction data for models of some of the more representative silicates, *viz.*, zircon, olivine, diopside, muscovite, and sanidine, are presented. Photographs and diagrams are included.

F.J.Z.

Cadmium spot tests. F. P. DWYER. *Jour. Australian Chem. Inst.*, **5** [1] 32–40 (1938).—"Cadion 2B," 4-nitronaphthalenediazoaminobenzene, will detect one part of Cd in 50,000 of Zn or 5000 of any other common metal except Hg. See *Ceram. Abs.*, **16** [5] 162 (1937). H.H.S.

Comparative observations on the determination of silicic acid in soluble materials. W. v. TONGEREN. *Chem. Weekblad*, **34** [48] 774–77 (1937).—T. describes the various methods in use of which a modification of the ammonium method is the most convenient, only 1 g. of a finely powdered sample being required and a very pure SiO_2 being precipitated. The exact procedure is described. M.H.

Determination of beryllium and aluminum. A. C. *Rev. Matériaux Construction Trav. Publics*, No. 333, p. 95B (1937).—The method is based on the quantitative separation of Be in acetic medium by precipitating it with alkaline phosphates in the state of phosphates of Be and of ammonium. The precipitate is filtered, washed, dried, and calcined as pyrophosphate of Be. Mg is precipitated by *o*-oxyquinoline in ammoniacal medium. Cobalt and nickel, if present, are eliminated simultaneously with the iron. The presence of Cr does not interfere with the determination of Al and Mg, but it hampers the determination of beryllium. M.V.C.

Determination of chromium in chromite. Procedure employing a mixture of phosphoric, sulfuric, and perchloric acids. G. FREDERICK SMITH AND C. A. GETZ. *Ind. Eng. Chem., Anal. Ed.*, **9** [11] 518–19 (1937).—A rapid method for the solution of all types of chromite ore, using a mixture of phosphoric and sulfuric acids, is described. After solution in mixed phosphoric and sulfuric acids, the chromium is oxidized, using concentrated perchloric acid at 215°C, and is treated for a brief time with potassium permanganate. In the determination of hexavalent chromium, standard ferrous sulfate is used with ferroin as indicator. The new process was used for the analysis of 13 samples of chromite and chrome refractories from a wide variety of sources, and no exceptions to its applicability were found. The method is rapid, accurate to within less than 2 parts per thousand, and not costly. F.G.H.

Determination of copper, zinc, and lead in silicate rocks. E. B. SANDELL. *Ind. Eng. Chem., Anal. Ed.*, **9** [10] 464–69 (1937).—S. describes a colorimetric method for the determination of the small amounts of copper, zinc, and lead occurring in rocks, which is based on the use of dithizone (diphenylthiocarbazone, phenylazothionoformic acid, phenylhydrazide), a reagent which is well suited for the purpose because of its great sensitivity. The procedure developed is based on the investigations of Hellmut Fischer (*Ceram. Abs.*, **13** [7] 193 (1934)) and others on the use of dithizone for determining traces of heavy metals. The sample is decomposed with hydrofluoric-perchloric acid and sodium carbonate, and the resulting solutions are extracted with a carbon tetrachloride solution of dithizone in a slightly basic medium in the presence of citrate. Copper, zinc, and lead form dithizonates which dissolve in the carbon tetrachloride, whereas the major constituents of the rock remain in the aqueous phase. The carbon tetrachloride layer is separated and shaken with 0.01*N* hydrochloric acid, whereby the dithizonates of zinc and lead are decomposed, giving the chlorides of these metals in the aqueous phase; the copper complex is not decomposed by the dilute acid and remains in the carbon tetrachloride. The latter is evaporated to dryness, and the residue is ignited to cupric oxide which is dissolved in hydrochloric acid; the copper in this solution can be determined by extractive titration with dithizone-carbon tetrachloride at a p_H of approximately 3.5 or by mixed-color colorimetry with the same reagent in acid solution. The 0.01 *N* hydrochloric acid solution containing the zinc and lead is made up to volume, and the two metals are determined colorimetrically in separate aliquots with dithizone: zinc by the mixed color technique at a p_H of about 4.1 in the presence of thiosulfate to prevent the interference of lead; and lead in an ammoniacal solution containing potassium cyanide to prevent the reaction of zinc. Illustrated.

F.G.H.

Determination of lead on water. J. W. HAWLEY AND W. WILSON. *Analyst*, **62** [732] 166–72 (1937).—Two methods, one electrolytic, the other concentration, are described. The electrolytic method is recommended for the highest precision and when the water is contaminated

with other metals. (*1*) *Electrolytic:* The Pb is precipitated as sulfide in the presence of excess Cu salts at p_H 4 to 5. The mixed sulfides are filtered and washed with saturated H_2S water. The filter paper is destroyed by a wet combustion. Pb is electrolyzed as PbO_2; this deposit is dissolved from the electrode, and Pb is estimated colorimetrically as sulfide. (*2*) *Concentration:* The water is acidified and concentrated to a small volume. Organic matter is oxidized by $KClO_3$ and HCl. Pb is precipitated as sulfide at p_H 4 to 5. The filtered sulfide, washed, is dissolved in concentrated HNO_3. The solution is evaporated to dryness with H_2SO_4 to destroy filter paper fiber if present. $PbSO_4$ is dissolved in boiling ammonium acetate, and, after filtration, Pb is estimated colorimetrically as sulfide. H.H.S.

Determination of uncombined lime in Portland cement. The ethylene glycol method. D. R. MacPherson and L. R. Forbrich. *Ind. Eng. Chem., Anal. Ed.*, **9** [10] 451–53 (1937).—The applicability of the ethylene glycol method of Schläpfer and Bukowski to the determination of uncombined calcium oxide or hydroxide in Portland cements, clinkers, and hydrated cements was studied. When modified, the ethylene glycol method, which requires only 40 min. for a complete determination, is satisfactory for determining uncombined calcium oxide in clinker and Portland cement and may be substituted for the glycerol alcohol method which requires from 1 to 7 hr. for completion. The ethylene glycol method can not be recommended for determining uncombined calcium hydroxide in hydrated Portland cement because, in the older samples, it is not completely dissolved, presumably on account of its coarsely crystalline state and because hydrates of the alumina compounds decompose in the presence of ethylene glycol. Illustrated. F.G.H.

Determining moisture content in refractory and other materials by the distillation method. P. I. Dolinskiĭ. *Zavodskaya Lab.*, **6**, 633–34 (1937). P.B. & E.S.

Device to determine the oxygen content of the air. A. Romwalter. *Magyar Kir. József Nádor Müszaki és Gazdaságtudományi Egyetem Bánya-, Kohó- és Erdőmérnöki Kar, Sopron. A bánya és kohómérnöki osztály Közleményei*, **9**, 89–92 (1937).—A more convenient modification of the Lindemann-Winkler apparatus is described which, after 3 min. of taking the air sample, permits the reading of the O content with an accuracy of 0.1%. M.H.

Direct determination of aluminum oxide in silicates. P. N. Grigor'ev and V. G. Dubovitzkiĭ. *Ogneupory*, **5** [2] 105–11 (1937).—A method for a direct determination of aluminum oxide in silicates, in particular in refractories, has been developed. It is based on a gravimetric determination of alumina by means of its precipitation with ammonia from the filtrate obtained after the separation of iron with caustic alkalis. The volumetric determination consists in the determination of alumina from the same filtrate, after neutralizing it with hydrochloric acid, and by titrating it with a titrated solution of limewater and phenolphthalein. M.V.C.

Effect of heating upon the exchange capacity of soils. Yutaka Kamoshita. *Jour. Sci. Soil Manure, Japan*, **11**, 343–48 (1937); *Chem. Abs.*, **31**, 8091 (1937).—Changes in base-exchange capacity of soils heated to 100° to 800° depended on the molecular ratios of SiO_2 to Al_2O_3 and to $Al_2O_3 + Fe_2O_3$ of the soil.

Effect of various gases on the course of the reaction between zinc oxide and chromic oxide. Gustav F. Hüttig, Suzanne Cassirer, and Erich Strotzer. *Z. Elektrochem.*, **42** [5] 215–22 (1936).—A study of the intermediate states in the reaction between ZnO and Cr_2O_3 in the presence of NH_3, A, H_2O, CH_3OH, N_2O, and air was made by heating stoichiometric mixtures of the solids to temperatures from 50° to 500° and observing the hygroscopicity, color, and magnetic properties of the quenched melts. The series of measurements was compared with measurements *in vacuo*. *In vacuo* a first phase holding up to 250° is characterized by a drop in hygroscopicity. A second phase of activation resulting from a formation of a surface layer of Cr_2O_3 on the ZnO shows a drop in water-binding power and a fall in magnetic susceptibility. This is followed by a period of inner diffusion of the Cr_2O_3 where hygroscopicity increases and magnetic susceptibility falls. Above 400° a period is noted where crystals of $ZnCrO_4$ form. All of the added gases exerted an effect on the magnitude of these changes and the temperature at which they occurred due to adsorption, but there was nothing systematic in the effects. The behavior of such intermediate states as mixed catalysts was discussed. E.J.V.

Free two-dimensional crystals of silicon pentoxide. N. A. Shishakov. *Phil. Mag.*, **24**, 687–95 (1937); see *Ceram. Abs.*, **16** [11] 358 (1937). C.J.P.

Inversion of quartz to tridymite: VI–VIII. S. Kondo, T. Yamauchi, and Y. Kora. *Jour. Soc. Chem. Ind. Japan*, **40** [6] 214–15B (1937).—The thermal expansion of tridymite and cristobalite and the thermal reaction and residual expansion of cristobalite were studied. **IX–XII.** *Ibid.*, [7] 233–35B. **XIII–XIV.** S. Kondo and T. Yamauchi. *Ibid.*, [8] 281–82B.—The production of silica brick and some physical properties of these brick are dealt with. For Parts **III–V** see *Ceram. Abs.*, **15** [4] 134 (1936). M.V.C.

Isomorphism and oversaturation. L. J. Klinkenberg. *Chem. Weekblad*, **34** [39] 617–19 (1937).—The principles of isomorphism are briefly explained, and recent developments of its conception are surveyed. K. shows that the X-ray analysis of crystals has made it possible to give an exact definition, *viz.*, that isomorphous compounds must belong to the same type, the ratio of their dimensions must not be too different, both elementary cells must have the same amount of positive and negative atoms in groups of atoms, and these atomic groups must occupy geometrically analogous places in the elementary cell. The old definition for isomorphism, *i.e.*, mixability and the prevention of oversaturation, is no longer valid. Examples of isomorphous crystals with lattice dimensions are given in a table. M.H.

Latent heat of fusion. N. S. Binavendra. *Gazz. Chim. Ital.*, **67** [11] 714–15 (1937).—According to B.'s experiments, the latent heat of fusion can be expressed by the formula $L = K \times Y^{3/4}$, where Y is the surface tension and K is a constant, dependent on the nature of the lattice structure, varying between 0.78 and 1.09. A table gives the constant for a number of elements. M.H.

Measurement of strain in opaque bodies. H. Schulz.

Glastech. Ber., **15** [8] 301–306 (1937).—Strains in certain bodies are best determined by effects on their optical constants. When the state of strain can be reproduced exactly by external forces, a transparent model can be used in the study of opaque bodies. Thermal strains in opaque bodies can be detected by rotation of the plane of polarization of light reflected from the surface. The accuracy with suitable experimental conditions is sufficient for practical purposes. J.F.H.

Microanalysis of silicates. F. HECHT. *Mikrochim. Acta*, **2**, 188–208 (1937); *Chem. Abs.*, **32**, 881 (1938).—Complete directions for analyzing silicates and determining SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O, CO_2, TiO_2, P_2O_5, S, and MnO are given. H. recommends the use of 8 samples of each mineral, each weighing 10 to 20 mg. In the first only SiO_2 is determined. The second sample serves for Al_2O_3, total Fe, CaO, MgO, TiO_2, and MnO. The third sample serves for determining water below 110° and for P_2O_5. The fourth sample is for water above 110°, the fifth for total S, the sixth for Na_2O and K_2O, the seventh for FeO, and the eighth for CO_2. Typical results obtained with five minerals are tabulated, and the results compare favorably with those obtained in the usual way with samples 100 times as large.

Microchemical test for selenium. M. HARRISON EVANS. *Amer. Mineralogist*, **22** [11] 1128–30 (1937).—The new test, using thiourea ($SC(NH_2)_2$), has the advantage that the very highly colored product is distinctive, and by observing certain precautions, it is specific and not interfered with by other elements in the test solution. F.J.Z.

Microdetermination of carbon and hydrogen. ADALBERT ELEK. *Ind. Eng. Chem., Anal. Ed.*, **10** [1] 51–52 (1938).—E. describes experiences in the microdetermination of carbon and hydrogen with suggestions and modifications as to the method and technique. The technique, using two boats and two capillaries, has contributed to the accuracy of carbon and hydrogen determinations for easily subliming or volatile substances. F.G.H.

Micromethod for determination of melting points. B. MEZENER AND S. WEHRLI. *Helv. Chim. Acta*, **18** [6] 1281–83 (1935).—A description is given of a method which avoids loss of valuable material, especially in the toxicological field where only very small amounts are available. E.W.S.

Possibilities of spectroscopy. P. SWINGS. *Rev. Universelle Mines*, **11** [8] 276–80 (1935).—S. shows the parallel development of theoretic spectroscopy and knowledge of the constitution of matter, the position of the spectral rays being in relation to the atomic or molecular energies, *i.e.*, to the electronic distributions, the vibrations within the molecule, and the globular rotation of the latter. The interpretation of the spectra of elements has opened up the road to highly interesting researches in astrophysics and physicochemistry. Moreover, spectroscopy, which permits the making of qualitative and even quantitative analyses, begins to render the greatest services in the arts. Several examples of such analyses, as well as pictures and references, are given. E.W.S.

Precision gas analysis. W. F. FULTON. *Refiner & Natural Gasoline Mfr.*, **16** [6] 284–87 (1937).—F. describes instruments and materials used in the analysis of natural gas. The checking of recording calorimeters, with a constructed precision calorimeter similar to the one used by the Bureau of Standards, is also described. J.J.H.

Progress in the field of gas analysis. H. VAN DAM. *Ing. chim.*, **21**, 94–118 (1937); *Chem. Abs.*, **31**, 8259 (1937).—A sturdy Orsat apparatus is made with pipets suspended from a Pyrex capillary manifold by means of rubber connections. The free end of the absorbing bulbs is covered with a small rubber sack to keep out the outside air, except that bulb containing Br water, which has a layer of paraffin oil floating over the water. Preparation of the solutions, particularly CuCl, and a description with a drawing of the combustion process are given. In burning CH_4, the CO_2 formed must be removed each time before the gas is repassed over the CuO, as CH_4 does not burn completely in the presence of CO_2. Under proper conditions the analysis should be completed in $^1/_2$ hr. The apparatus is cleaned, after dismounting, with 5 to 10% HF; contact of the solution with the ground surfaces is to be avoided. A portable apparatus for analysis of gas by fractional condensation is described. The Pyrex apparatus, joined without any rubber connections, has a mounting for 4 U tubes in a square which can be cooled with liquid air or liquid O. The Dewar flasks are mounted with a rack and pinion. For other temperatures, Al blocks cooled to the desired temperature give remarkably constant temperatures. Details of the process and methods of analysis are given. An apparatus for taking a mean sample of gas from the main conduit, over a period of 24 hr., the amount taken to be proportional to the total flow, consists of a suction pump whose silica valves are covered with Hg and controlled by a magnet operated by an electric flowmeter. The magnet also controls the stopcocks of the pump. A floating bell jar constitutes the piston. When the current is broken, a spring returns the bell jar to its initial position, at the same time forcing the gas collected in it out through another valve into the gasometer. A detailed description with 3 drawings of the apparatus is given.

Qualitative metallographic X-ray technique. A. J. BRADLEY. Read before International Association for Testing Materials, London, April, 1937; *Sheet Metal Ind.*, **11** [122] 573 (1937).—B. presents a brief account of the development of methods for obtaining accurate lattice spacings and improvements in the measurement of X-ray intensities from powder photographs. A.P.S.

Quantitative separation of iron, aluminum, and chromium from the other members of the ammonium sulfide group. G. CHARLOT. *Bull. Soc. Chim.*, [5] **4**, 1235–44 (1937); *Chem. Abs.*, **31**, 6996 (1937).—Of the various cations in Group III, Fe^{+++} begins to precipitate below $p_H = 4$, and at $p_H = 5.4$ less than 0.1 mg. of Fe remains in 100 ml. of solution. Al is incompletely precipitated at $p_H = 4.9$ but less than 1 mg. Al remains in solution at $p_H = 5.4$. Cr is not precipitated at p_H below 6.2 in the absence of Fe^{+++}, but in the presence of Fe^{+++} it is thrown down incompletely with the Fe; if less than 20 mg. of Fe^{+++} is present, the Fe^{+++} is kept in solution by the Cr^{+++}. The presence of 0.2 g. of Fe^{+++} causes the precipitation of 0.25 g. of Cr^{+++} at p_H 5.4, and about 2 mg. of Cr remains dissolved in 100 ml. of solution. With respect to precipitation of 0.1 to 0.01 *M* solutions at slowly increasing p_H, Sn^{++} and Zr precipitate at $p_H = 2$; Hg^+, Th, Fe^{+++}, and Ti at p_H 4.3; Al at p_H 4.9; U, Cr, Cu,

and Zn at p_H 6.4; Ag and Be at p_H 6.5; Co, Ni, Fe^{++}, Cd, Hg^{++}, Pb, and Mn at p_H 8.4; Mg at p_H 10.5; Tl^{+++}, Ce, Ga, U^{++++}, Ta, and Cb precipitate before Fe^{+++} and the rare earths are thrown down at p_H 6.5 to 8.0. At p_H 5.4 the separation of Fe-Zn; Fe, Al-Ca, Mg; Al-Ce, Fe, Al-Co, Fe-Ni; and Fe, Al-Mn is nearly quantitative (to within 1 mg.) but a double precipitation is necessary for Al-Zn, Al-Ni, and Fe-Ce. The results are fairly satisfactory in the difficult separation of Al-Zn. If the ratio of Fe:Cr is at least 1, the separation of Al, Cr, and Fe from Zn is fairly satisfactory. In the filtrate, Zn, Ni, and Co can be precipitated as sulfides at the same p_H, and Mn remains in the filtrate. Above 0.1 mg. of Mn is thrown down with precipitated sulfides at p_H 5.4.

Slag systems: FeO–Al_2O_3 and FeO–MnO–Al_2O_3. R. Hay, A. B. McIntosh, J. R. Rait, and J. White. *Jour. West Scot. Iron & Steel Inst.*, **44** [6] 85–92 (1937).—*System FeO–Al_2O_3*: a eutectic temperature of 1305°C corresponding to a composition of 5% Al_2O_3 and 95% FeO was found; the formation of $3FeO \cdot Al_2O_3$ from $FeO \cdot Al_2O_3$ and FeO occurred at 1225°C; transformation takes place very slowly; the fluidity of the melts was high for small percentages of Al_2O_3 and decreased rapidly as the Al_2O_3 content was increased beyond 5%. *System FeO–MnO–Al_2O_3:* a diagram shows no true ternary eutectic point; an invariant point was found for a composition of 20 Al_2O_3, 40 MnO, and 40% FeO; in the dissociation of Fe_2O_3, the ratio of $\frac{FeO}{Fe_2O_3}$ is decreased with increasing amounts of CaO and O_2; the ratio is increased with increased temperature and increasing percentage of SiO_2. B.C.R.

Supplement to "A compilation of phase-rule diagrams of interest to the ceramist and silicate technologist." F. P. Hall and Herbert Insley. *Jour. Amer. Ceram. Soc.*, **21** [4] 113–66 (1938); see *ibid.*, **16** [10] 455–568 (1933).

Temperature-viscosity relationships of coal slags: I, Methods of investigation and results. K. Endell and C. Wens. *Z. Ver. deut. Chem.* (*Beiheft*), No. 12; abstracted in *Angew. Chem.*, **48**, 76–77 (1935).—Temperature-viscosity relationships of coal slags and synthetic mixtures of the quaternary system SiO_2–Al_2O_3–Fe_2O_3–CaO were measured, and various graphs are given. Since the absolute measurements of the viscosity require complicated devices, measurements of relative viscosity by means of the grooved viscosimeter permitted measurement of the flowing periods of the slags resulting from the ashes in dependence on the temperature. For higher viscosities it was more convenient to observe the slumping of the ash cone by means of a telescope with micrometer ocular. **II, Conclusions for the firing techniques.** P. Rosin and R. Fehling.—By measuring the viscosity of the slags, the range of temperature of the pasty state to be avoided in practice may be limited. The temperature of the start of the drop formation of the slag is important, since, when forming drops, the slag will endanger the grate surface. The measurements of viscosity will serve to determine in what case and to what extent the ashes may be removed mechanically in the dry state or in the form of liquid slags. E.W.S.

Ternary and quaternary systems alkali oxide–CaO–SiO_2–CO_2. Equilibria, reaction velocities, and their relation to the glassmelting process: I. C. Kröger. *Glastech. Ber.*, **15** [9] 335–46 (1937).—A critical review of the subject is presented. 113 references. **I** (continued). *Ibid.*, [10] 371–79.—Equilibria in the systems Li_2O–SiO_2–CO_2 and K_2O–SiO_2–CO_2 are considered. J.F.H.

Ternary system. M. Moray. *Rev. Universelle Mines*, **11**, 141–52 (March, 1935).—M. gives a critical review of researches and experimental methods for the determination of the fusibility of slags with respect to the ternary system FeO–CaO–SiO_2 and the establishment of the ternary equilibrium diagram. He states that frequently, due to special economic conditions in each factory, a slag of imperfect composition will have to be satisfactory. 33 references. E.W.S.

Versatile nomograph for chemical engineering calculations. E. L. McMillen. *Ind. Eng. Chem.*, **30** [1] 71–74 (1938).—A nomographic chart is described which makes possible direct multiplication and division by numbers raised to any power. With this chart it is possible to solve directly a large variety of equations involving fractional exponents which are encountered in chemical engineering calculations, thus saving considerable time as contrasted to slide rule or logarithmic computations. Accuracy of computation with this chart has been found comparable to that obtained with the slide rule. A combination of a slide rule with a nomographic chart embodying the same principle is described. Illustrated. F.G.H.

Volumetric determination of selenium. Critical study of the Norris and Fay method. W. C. Coleman and C. R. McCrosky. *Ind. Eng. Chem., Anal. Ed.*, **9** [9] 431–32 (1937).—Using pure selenium as a primary standard, the accuracy of the Norris and Fay method was found to be between 1 and 2 parts per 1000. This titration can be carried out at room temperature if a small excess of thiosulfate solution is used. A rapid method for controlling this excess is described. This modification results in a considerable saving of time in the use of this method. For accuracy, only a small excess of thiosulfate solution should be used. Hydrobromic, sulfuric, perchloric, and hydrochloric acids can be used in the Norris and Fay procedure. F.G.H.

PATENTS

Alkali silicate. "Montecatini." Soc. gen. per l'industria mineraria ed agricola. Fr. 811,621, April 19, 1937; *Chem. Abs.*, **32**, 736 (1938).—A solid alkali silicate which readily dissolves at ordinary temperature and pressure is made by dissolving ordinary soluble glass in water at raised temperature and evaporating the solution obtained.

Alkaline earth metals. Wilhelm Kroll. Fr. 811,487, April 15, 1937; *Chem. Abs.*, **32**, 736 (1938).—Alkaline-earth metals, particularly Ba, are prepared by heating an alkaline earth, *e.g.*, BaO, with V, Ni, Ta, Ce, or U or mixtures thereof, under a high vacuum. The BaO may be partly replaced by BaS.

Anhydrous water-soluble silicates and method of preparing. L. T. Howells, A. W. Scheidt, and H. B. Williams (Electric Smelting and Aluminum Co.). U. S. 2,110,363, March 8, 1938 (Dec. 22, 1933). The method of preparing basic silicates of the anhydrous alkali metal silicate type comprises preparing a fused mass of such material containing from $^3/_4$ to $1^1/_2$ mol. of alkali-metal oxide

to 1 mol. of silica and chilling the material by artificial means through its critical temperature range to a temperature below approximately 1000°F within a period of about 5 sec., thereby forming a substantially transparent solid product which is substantially free from opaque crystalline material relatively insoluble in an aqueous solution of the transparent product.

Luminescent material. H. W. LEVERENZ (Radio Corporation of America). U. S. 2,110,161, March 8, 1938 (Jan. 31, 1935). A metallic orthogermanate activated by rhenium which gives to the combination the characteristic of becoming luminescent upon being excited by "radiant energy."

Luminescent material. H. W. LEVERENZ (Radio Corporation of America). U. S. 2,110,162, March 8, 1938 (Jan. 31, 1935). A metallic orthogermanate activated by a metal of the second subgroup of the first vertical column of the periodic system which gives to the combination the characteristic of becoming luminescent upon being excited by irradiations of "radiant energy."

Method of preparing TiO_2. R. H. MONK AND A. S. ROSS (American Zinc, Lead & Smelting Co.). U. S. 2,108,723, Feb. 15, 1938 (Nov. 11, 1935). In a process of preparing titanium dioxide, the steps comprise forming an aqueous and approximately neutral dispersion of a protective colloid and a salt relatively insoluble in water but completely soluble in the aqueous medium resulting from hydrolysis and then adding a concentrated titanium salt solution thereto.

Preparation of a zirconium oxycarbide and silicon carbide. C. J. KINZIE AND D. S. HAKE (Titanium Alloy Mfg. Co.). U. S. 2,110,733, March 8, 1938 (March 1, 1934). (5) The method of converting zircon, containing compounds of iron and titanium as impurities, mixed with carbon-containing material into a zirconium compound essentially free of silicon, titanium, and iron but mixed with silicon carbide, comprises heating, without fusion but with substantial decomposition, the charge enveloped in a carbonaceous insulating mix in an electric resistance furnace to form a dark-colored powdered zirconium compound containing a relatively small amount of the silicon carbide. (7) A zirconium compound containing zirconium, carbon, and oxygen and probably having the structural formula (ZrO·C) obtained by high-temperature decomposition without fusion of zircon, containing compounds of iron and titanium as impurities, mixed with a carbonaceous material, the compound being characterized as an opaque black powder of particle size from 0.005 to 0.03 mm., substantially free of silicon and iron, and with less than $\frac{1}{2}$ of 1% of titanium as an impurity.

Process of separating beryllium compounds from aluminum compounds. C. E. WHITE AND P. A. PARENT. U. S. 2,110,010, March 1, 1938 (June 18, 1937). The process of separating aluminum from beryllium in acid solutions of the two comprises precipitating substantially all of the aluminum by the addition of sodium hexametaphosphate.

Sodium silicate adhesives. A. S. WEYGANDT (E. I. du Pont de Nemours & Co.). U. S. 2,111,131, March 15, 1938 (Feb. 29, 1936).

Treatment of alumina-magnesia-chromite ore. A. E. GREENE. U. S. 2,110,573, March 8, 1938 (June 8, 1936). The method of treating chromite containing substantial percentages of alumina and magnesia to separate the latter in substantially pure and unadulterated condition and to recover the chromium as an iron alloy consists in preparing a charge of the ground chromite-alumina-magnesia material together with carbonaceous reducing agent in sufficient amount to reduce substantially all of the chromium and iron oxides present, the carbonaceous material being substantially free from any agent which would materially lower the melting point of the unreduced remaining alumina-magnesia, reducing this charge in an arc chamber and causing fusion of the reduced metal and of the alumina-magnesia by means of the arc heat, cooling the charge, and separating the metal and alumina-magnesia products from one another.

General

Ceramic industry of West-Steirmark. F. SCHWARZ. *Sprechsaal*, **70** [40] 505–507; [41] 515–17 (1937).—The region of West-Steirmark, in the south of Austria, is well suited for the development of the stoneware, whiteware, and ceramic building materials industries. It has rich deposits of various high-grade raw materials, coal, and water power. The deposits of raw materials are described. M.V.C.

Dangerous dust and fumes—cause of industrial diseases. F. M. R. BULMER. *Can. Machinery*, **48**, 27–29 (1937); *Chem. Abs.*, **31**, 7142 (1937).—On the basis of the hazards involved, four classes are discussed. The so-called harmless dusts contain no silica. In heavy concentrations they cause irritation of the nose and throat and swelling of the lining of these and adjacent organs. Limestone is an example. Skin-irritating substances include acid and alkali fumes, dusts of Cr compounds, and certain Pb compounds, particularly tetra-ethyl lead. Definitely poisonous substances include Pb, As, and Cd dust. Skin trouble and erosion of the nose partition may be caused by As. Even minute quantities of Cd are very dangerous. Dusts producing scarring of the lungs (fibrosis) are usually those containing silica. Particles of 1 to 10 microns are most effective in producing silicosis which, if advanced, often develops into tuberculosis.

Financial statements calculated for short periods in hollow glass factories. H. OTTEN. *Glastech. Ber.*, **15** [8] 308–13 (1937). J.F.H.

Fine-dust filter—the problem and its solution. G. STAMPE, K. GROSSKOPF, AND K. F. MÖLLERING. *Draeger-Hefte*, No. 191, pp. 3571–82 (1937); *Chem. Abs.*, **31**, 7701 (1937).—The occurrence, characteristics, and danger of fine dusts are discussed. Fine dusts are defined as dusts composed of particles less than 1 micron in diameter. Coarse dust is composed of particles between 1 and 3 microns in diameter. Several methods for the determination of particle size are described. Coarse dusts are easily caught by a filter of cotton or other fibers. Fine dusts require a specially constructed filter, such as that constructed by the Draeger Co., which has been thoroughly tested against several types of fine dust. It is designated "fine dust filter df 90." It has a prefilter of loosely pressed

fibers and an accordion filter of specially prepared filter paper. This filter has an efficiency factor of 99.85% when tested against fine stone dust and silica dust. Numerous photomicrographs of dust collected from air before and after passing through this filter are shown. Several photographs of the filter and its construction and of apparatus used in measuring particle diameter are also given. Excellent checks are obtained by several different methods of measurement.

Germ invasions in houses fought by means of vitrified and enameled ceramic products. F. CHALAMEL. *Céramique*, **41** [598] 1–9 (1938).—On the basis of experiments, C. found that vitrified ceramic linings or enameled coats present considerable advantages in fighting germs. The importance of the composition of floors and materials used for walls on the development and propagation of germs was studied. One of the most important factors is the easy condensation of humidity as water drops on cold walls coated with ceramic products. M.V.C.

Health hazard of a group of workers exposed to alumina dust. CHARLES L. SUTHERLAND, A. MEIKLEJOHN, AND F. N. R. PRICE. *Jour. Ind. Hyg. & Toxicol.*, **19**, 312–19 (1937); see "Silicosis risks—," *Ceram. Abs.*, **17** [2] 89 (1938). E.J.V.

Present status of ceramic engineering curricula. Report of Curricula Committee of the Association of Ceramic Educators. M. E. HOLMES, Chairman. *Bull. Amer. Ceram. Soc.*, **17** [3] 135–40 (1938).

Prevention of silicosis by metallic aluminum. ANON. *Aluminium*, **20** [1] 47 (1938).—Laboratory experiments with guinea pigs resulted in the conclusion that the addition of Al powder to quartz powder (SiO_2) prevents the dissolving of dangerous amounts of SiO_2 in the lung tissues, thus causing silicosis. A practical method for the use of the discovery has not been found; naturally, inhalation of Al powder can be no practical solution. See "Aluminum—," *Ceram. Abs.*, **17** [1] 46 (1938). M.H.

Report of Committee on Ceramic Education. A. F. GREAVES-WALKER, Chairman. *Bull. Amer. Ceram. Soc.*, **17** [3] 140–41 (1938).

Report of Committee on Standards. J. W. WHITTEMORE Chairman. *Bull. Amer. Ceram. Soc.*, **17** [3] 141–45 (1938).

BOOK

A.S.T.M. Tentative Standards, 1937. Published by the American Society for Testing Materials, Philadelphia, Pa. 1629 pp. Price to nonmembers $7.00 paper cover, $8.00 cloth cover. In this edition are 293 tentative specifications of which 37 apply to cementitious, ceramic, concrete, and masonry materials. R. A. HEINDL

NEW JOURNAL

National Physical Laboratory Abstracts of Papers Published in 1936. Department of Scientific and Industrial Research. H. M. Stationery Office, London, 1937. 65 pp. Price 1s. Official papers from the National Physical Laboratory published in various scientific and technical journals as well as by H. M. Stationery Office are abstracted. The *Abstracts* supplement the *Annual Report* and supersede the *Collected Researches* of the Laboratory. The *Abstracts* will be published annually. L. R. BARRETT

PATENTS

Ceramic materials. GEWERKSCHAFT KERAMCHEMIE-BERGGARTEN. Fr. 813,939, June 11, 1937; *Chem. Abs.*, **32**, 1065 (1938).—Ceramic materials prepared by a wet method but not liquid are degassed by the application of reduced pressure and heating to the boiling point of the liquid used. The density of the material is increased by the application of increased air pressure immediately after the degassing.

Connection between ceramic bodies and metals. R. SCHARFNAGEL. Brit. 479,084, Feb. 9, 1938 (July 25, 1935).

Porous ceramic bodies. "NAGYBÁTONY-UZLAKER" VEREINIGTE INDUSTRIEWERKE A.-G. Swiss 191,187, Aug. 16, 1937; Cl. 8*b*.; *Chem. Abs.*, **32**, 1065 (1938).—Highly porous bodies are made by molding a mixture of kieselguhr, slaked lime, water, and water-glass solution.

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